

TRANSDIMENSIONAL PLASMONIC TITANIUM NITRIDE FOR TAILORABLE NANOPHOTONICS

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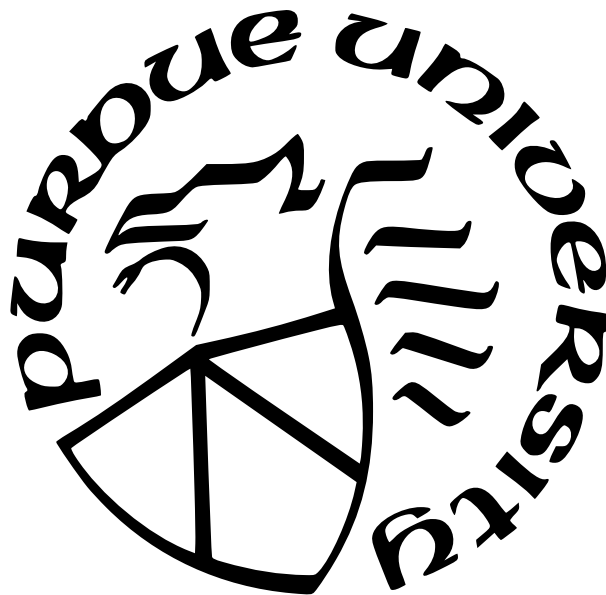
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To Mom, Dad, and Akhil

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ABSTRACT

In the realm of tunable optical devices, 3D nanostructures with metals and dielectrics have been utilized in a wide variety of practical applications ranging from optical switching to beam-steering devices. 2D materials, on the other hand, have enabled the exploration of truly new physics unattainable with 3D systems due to quantum confinement leading to unique optical properties and enhanced light-matter interactions. Transdimensional materials (TDMs) – atomically thin films of metals – can couple the robustness of 3D nanostructures with the new physics enabled by 2D features. However, the evolution of the optical properties in the transdimensional regime between 3D and 2D is still underexplored. The optical properties of metallic TDMs are expected to show unprecedented tailorability, including strong dependences on the film thickness, composition, strain, and surface termination. They also have an increased sensitivity to external optical and electrical perturbations, owing to their extraordinary light-confinement. Additionally, the small atomic thicknesses may lead to strongly confined surface plasmons and quantum and nonlocal phenomena. The strong tunability and light-confinement offered by TDMs have resulted in a search for atomically thin plasmonic material platforms that facilitate active metasurfaces with novel functionalities in the visible and near infrared (NIR) range. In this research, we explore the plasmonic properties and tailorability of atomically thin titanium nitride (TiN). We experimentally and theoretically study the thickness-dependent optical properties of epitaxial TiN films with thicknesses down to 1 nm to demonstrate confinement induced optical properties. Overall, this research demonstrates the potential of TDMs for unlocking novel optical phenomena at visible and NIR wavelengths and realizing a new generation of atomically thin tunable nanophotonic devices.

1. TRANSDIMENSIONAL PLASMONIC MATERIALS

Surface plasmons (SPs), which are optically induced oscillations of the electron cloud excited at metal-dielectric interfaces, enable strong light confinement beyond the diffraction limit and highly localized electromagnetic fields[1], [2]. Plasmonic nanostructures uniquely allow for light manipulation at the nanoscale and have been instrumental in advancing a range of applications [3], including photovoltaics [4], [5], optical circuitry [6]–[8], and imaging [9], [10]. Advancements in nanofabrication techniques have allowed for precise optimization of the optical response of plasmonic devices by controlling the properties of the material building blocks, as well as the structure dimensions and geometry at the nanoscale [11]. Moreover, the dynamic control of the plasmon resonances has been of great interest to produce tunable nanophotonic devices for optical switches [12], [13], sensing [14]–[16], and modulators [17], [18].

Plasmonic components are typically made up of metals, such as gold or silver, due to their low losses and high conductivity [19]. However, because of their large charge densities, the penetration of electromagnetic fields inside metals is very low. This low penetration depth, coupled with the high ohmic losses, makes appreciable optical tuning difficult with bulk metals [20], [21]. Additionally, noble metals are known to be extremely soft with a low mechanical and thermal stability, limiting their applications for harsh environment devices. Noble metals’ softness, lack of tunability, and low melting point, along with challenges in thin film fabrication, have prevented the realization of practical plasmonic devices requiring tailorable optical properties and durable metallic nanostructures. In response to these pressing requirements, investigations into new plasmonic materials that meet the need for tunable and robust nanophotonic devices have increased.

Emerging plasmonic materials, such as transparent conducting oxides (TCOs) [22]–[25] and graphene [17], [26], [27], have been heavily investigated for their highly tunable response. In the case of TCOs, a low carrier concentration compared to bulk metals[24], [28] enables a greater field-penetration into the materials with lower optical losses. This enhances the light-matter interaction, resulting in strong modulation. On the other hand, due to the monolayer thickness of two-dimensional (2D) materials, large changes in the sheet carrier density are

easily attained [29]. In addition to their tunability, the strong quantum confinement in 2D materials has led to unique phenomena unattainable with conventional bulk plasmonic materials, including forbidden atomic transitions, strong nonlinearities, and highly confined plasmons [30], [31].

Similar to 2D materials, ultra-thin films in the transdimensional (TD) regime spanning a few atomic layers, known as transdimensional materials (TDMs), are expected to exhibit strong dependencies on structural and compositional properties, as well as extreme sensitivities to external optical and electrical perturbations [32], [33]. Additionally, the small atomic thicknesses may lead to strongly confined surface plasmons and unique quantum phenomena like forbidden atomic transitions and large nonlinearities[30], [34]. While many of these unique effects have been demonstrated in 2D materials like graphene, the plasmon modes of these materials are at lower frequencies in the mid-infrared (MIR) range, far from the technologically important near-infrared (NIR) and visible wavelengths. Metallic TDMs are highly promising for achieving similar quantum and nonlocal effects in the visible and NIR. The strong tunability and light confinement offered by TDMs has resulted in a search for atomically thin material platforms that facilitate active metasurfaces with novel functionalities in the visible and NIR range [32]. TDMs are highly promising for greatly advancing plasmonic functionalities through unparalleled tailorability, dynamic control, and exceptionally high localization of light.

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1.1 Optical Properties of TDMs

Several theoretical studies have revealed the strong thickness dependence of plasmonic films due to quantum size effects and their potential use in low loss plasmonics[35]–[43], many of them depending on density functional theory (DFT) calculations. As the number of

layers of the Au and Al films is reduced, the complex permittivity becomes highly anisotropic at longer wavelengths and also exhibit a decrease in losses[35], [37]. In the case of ultra-thin plasmonic TiN, we show that reducing the number of layers results in red shifts in the interband transitions causing changes in the optical properties[41]. The results from this study is discussed in further detail in Chapter 3. Additionally, monolayer Ag has been predicted to have a higher frequency dependent conductivity and lower losses than its bulk counterpart[42].

Along with DFT methods, there have also been analytical solutions proposed to describe the evolution of optical properties in ultra-thin metals and their nonlocal response. Quantum mechanical (QM) models have been developed by applying the solution of the Schrödinger equation to atomically thin metal layers[39], [43]. Furthermore, Echarri et al. applied the formulated QM models to graphene-metal heterostructures to demonstrate the quantum size effects on the plasmon dispersion and lifetimes as well as the viability of acoustic plasmons with monolayer gold and graphene systems[43].

A nonlocal Drude response model has also been developed based on the Keldysh – Rytova (KR) potential, which describes the Coulomb interaction between electrons in transdimensional plasmonic planar films[40]. The derived model provides a mathematical description of the nonlocal effects that result in the thickness dependent complex permittivity and Drude plasma frequency of ultra-thin plasmonic films. Using this nonlocal KR model, many remarkable electromagnetic (EM) properties of plasmonic TDMs have also been demonstrated. For example, the strong spatial confinement of the electron transport in TD films has been predicted to result in a resonance magneto-optical response. Moreover, when carefully tuned, the ultra-thin films of finite lateral size can become negatively refractive in the IR frequency range[44]. The nonlocal KR model has also been used to study the coupling between the ENZ modes in TDMs and dipole emitters, revealing large dipolar spontaneous emission enhancement, which can be precisely controlled by the thickness dependent plasma frequency of the TD films[45].

1.2 Strongly Confined Plasmons in TDMs

Highly doped graphene has long been established as a promising 2D material platform that can combine huge confinement and enhancement of the electromagnetic field with lower losses and large electrical modulation of its optical properties[17], [27], [46]. However, due to their lower carrier densities, the strongly confined plasmons in graphene, as well as other 2D materials and topological insulators, lie at lower frequencies. In contrast, atomically thin metals support confined plasmons in the technologically important visible and NIR range because of their larger charge carrier density. As observed with plasmons in graphene, decreasing the thickness d of metallic films down to a range of just few atomic layers, results in a significant reduction of the in-plane surface-plasmon wavelength λ_p . In the Drude model, λ_p is related to d and the wavelength of light λ_0 as

$$\lambda_p = \frac{d\lambda_0^2}{L_1^2}$$

where L_1 is a characteristic length that depends on the combination of metal and substrate materials[47].

Advancements in thin film growth have resulted in many material choices to study these confinement effects on the plasmonic behavior in atomically thin metals and characterize the strongly confined plasmons in the visible and NIR in TD plasmonic structures. Quantum well states have been characterized in epitaxial silver films of 10 monolayers[47]. The layer dependent quantum well binding energies reveal trends characteristic of a 1-D particle in a box. In terms of the plasmonic properties, narrow, strongly confined plasmons at NIR wavelengths were measured in the silver films patterned into nanoribbons. Highly confined low dimensional plasmons have also been characterized in monoatomic gold wires[48] as well as ultrathin, continuous silver thin films[49].

According to a recent theoretical prediction, the transition rates of various forbidden transitions in atomic physics, such as electron spin-flips and multi-plasmon spontaneous emission, can be greatly enhanced by several orders of magnitude by using these strongly confined plasmons in TDMs [30]. Due to the large momentum mismatch between the photon momentum and the orbital angular momentum of the electron, transitions involving

changes in the orbital angular momentum of electrons are often considered to be impossible in light-matter interactions. For instance, the transition rates that change the orbital angular momentum of electron by n scale as $\alpha(ka_0)2n$, where α is the fine structure constant, a_0 is the characteristic size of the atom and k is the wavenumber of the photon. Due to the small size of atom a_0 the lifetimes of these transitions are quite large. However, using tightly confined plasmons in ultra-thin plasmonic films, where the plasmon wavenumber is larger than the free space wavenumber by several orders of magnitude, these transition rates can be greatly enhanced by several orders of magnitude, reducing the lifetimes to experimentally observable sub-micron timescales for transitions in the visible and NIR.

1.3 Confinement Enhanced Optical Nonlinearities

In bulk materials, the nonlinear response is dominated by the interband transitions, i.e. when an electron transitions from the d-band (valence band) to the s-band (conduction band). Due to quantum confinement in atomically thin metals, free electrons of the metal are quantized into subbands or discrete energy levels within the conduction band. Therefore, there are also intersubband transitions, which enhance the nonlinear response. The dipole transition elements associated with transitions between intersubbands are on the same order of magnitude of the quantum well thickness: $\mu_{mn} = E(\cos\alpha)\langle e_m|qz|e_n\rangle$, where z is the thickness of the quantum well, which is typically a few nanometers. On the other hand, the dipole transition elements for interband transitions are on the same order of magnitude as the interatomic distance: $\mu_{mn} = E\langle e_m|e_n\rangle\langle u_c|qr|u_v\rangle$, which is typically a few angstroms[50]. The larger dipole transition moment for intersubband transitions leads to a significantly larger $\chi^{(3)}$ value,

$$\chi^{(3)} = \frac{N(\mu_{mn}^4)}{(\omega_{mn} - \omega - i\gamma_{mn})^3}$$

The addition of new resonant terms in the permittivity due to quantum confinement results in an enhanced nonlinear response. The third order nonlinearities in TiN films have been characterized, and it has previously been shown that such nonlinearities can be increased for thinner films [51]. Specifically, in the Drude tail of the material where there is no nearby resonant term, quantum size effects may result in substantial enhancement and

modification of the nonlinearity by allowing energy level quantization, whose spectral location can be tuned with the thickness and/or coupling with other layers to coincide with a wavelength of interest. The ability to engineer the position of such a resonance would be a breakthrough in integrated nonlinear optics, allowing the material to be tailored to the wavelength of interest instead of the wavelength being tailored to the material.

The third order nonlinearities in ultra-thin gold films with thicknesses 3 and 15 nm grown in quartz have been studied using Z-scan measurements[34]. They demonstrate that the 3 nm thick gold quantum well has a $\chi^{(3)}$ value that is four orders of magnitude larger than the ones for bulk, 15 nm, and 20 nm films. Additionally, due to some weak confinement, the 15 nm and 20 nm films are slightly larger than that for bulk. The study provides further evidence to show that the enhanced nonlinearity is a purely quantum effect by measuring the wavelength dependent Kerr response, demonstrating that the resonances in the Kerr response (740 nm and 900 nm), correspond to the energies required for intersubband transitions in the metallic quantum well.

In addition to enhanced third order nonlinearities, TD metallic films may also be utilized to achieve enhanced second harmonic generation[52]. Enhancement of the second harmonic generation using asymmetric semiconductor quantum wells has been widely demonstrated with wavelengths in the mid infrared range. Using metallic TDMs, significant enhancement can be realized in the visible to NIR range. Multilayers of TiN and alumina, which are essentially asymmetric coupled metallic quantum wells, have been introduced to realize extremely high $\chi^{(2)}$ values at NIR wavelengths. The $\chi^{(2)}$ value of the TiN/ Al_2O_3 superlattice reported is several orders of magnitude larger than traditional plasmonic structures. By combining the quantum well heterostructure with the large electric field enhancement offered by a nanostructured plasmonic metasurface, at a pulse intensity of 10 GW/cm^2 , a power efficiency of 10^4 for second harmonic generation (SHG) was achieved. This efficiency is higher by several orders of magnitude compared to previous studies investigating the second order nonlinearity of different structures at similar wavelengths.

1.4 Tuning the Properties of Metals

Transdimensional plasmonic films are predicted to have a greatly increased sensitivity to the local dielectric environment, strain, and external perturbations. Consequently, unlike conventional metals with properties that are challenging to tailor, atomically thin plasmonic materials exhibit optical responses that can be significantly engineered by precise control of their thickness, composition, and the electronic and structural properties of the substrate and superstrate[33], [40], [53]. This unique tailorability, unachievable with bulk or relatively thick metallic layers, establishes metallic TD films as an attractive material platform for the design of tunable and dynamically switchable plasmonic metasurfaces[54].

The tailorable plasmonic behavior of atomically thin gold and silver has been demonstrated by careful control of the thickness. In an experimental study with gold, the behavior of the plasmon dispersion in ultra-thin gold nanoribbons with width W and thickness of 3 nm deviated significantly from those with a 15 nm thickness. In a separate study, considerable redshifts in narrow, strongly confined plasmons at NIR wavelengths were measured in epitaxial silver nanoribbons with thicknesses ranging from 8 – 12 monolayers. In this thesis, we have focused on demonstrating the thickness dependent optical properties in TiN. Moreover, recently, a nonlocal Drude response model was derived to theoretically demonstrate that the plasma frequency of ultrathin metals acquires a thickness dependence, which will be discussed in Chapter 4 in terms of the experimental trends we observe in TiN.

Strain engineering is also a critical method to understand and control the optical behavior, as it enables modification of the energy band curvature and related quantities[53]. Below a certain critical thickness, an epitaxial thin film will retain strain induced by the substrate. The effects of strain are only felt for of a very thin layer of an epitaxial material near the interface of the super and substrate, as the stress relaxes for atoms farther from the interface. Thus, to properly quantify the effects of strain, it is important to successfully obtain single – crystalline, ultrathin layers, where the strain will uniformly affect the deposited material, drastically simplifying modeling and experimental extraction. In conjunction with the thickness dependence of TDMs, strain engineering epitaxial TD films offers a novel avenue to tailor the optical response of plasmonic materials.

Moreover, similar to 2D materials[55], [56], high sensitivity to external optical and electrical stimuli is expected in plasmonic TDMs, which could facilitate the realization of ultrathin plasmonic devices where the properties can be dynamically modulated[33], [57]. As recently predicted[33], the free carrier densities, and thereby the optical response itself, can be significantly tuned with conventional gating techniques, provided that the metal film is only a few monolayers in thickness. For example, the dynamic modulation of plasmonic resonances in atomically thin metals has been experimentally demonstrated in 3 nm thick gold nanoribbons[58]. A 200 nm wavelength shift in the plasmonic resonance was observed by applying voltage biases from -2 V to 2 V, compared to only a 50 nm wavelength shift in a 6 nm film. The manipulation of the local density of optical states has also been experimentally demonstrated by utilizing the field effect-induced optical permittivity modulation of an ultrathin TiN film in a TiN/SiO₂/Ag heterostructure [54]. As a result, the spontaneous emission rate, far-field emission intensity, and quantum yield of quantum dots embedded in the heterostructure can be modulated. Additionally, active tuning via electrical gating of surface plasmon resonances in transdimensional indium doped tin oxide (ITO), a low carrier density Drude metal, has also been demonstrated in the NIR range [59]. These results indicate strong potential for metallic TDMs as a material platform for dynamic plasmonic and nanophotonic components for switchable metasurfaces.

1.5 Material Platforms for Transdimensional Plasmonics

To explore the sought after transdimensional thickness regime, there have been several efforts to grow ultra-thin metallic films with various plasmonic materials, such as gold[60] and titanium nitride (TiN)[61], [62]. Until recently, experimental investigations of atomically thin plasmonic materials had been largely limited due to the challenges in growing ultra-thin metal films that are continuous and have low roughness. For example, at small thicknesses, thin films of noble metals, which are the typical material platform choice for plasmonic devices, suffer from high roughness and nonuniformity due to island formation[63], [64]. However, due to recent progress in deposition techniques, continuous and smooth thin films of gold, silver and TiN that maintain their metallic properties at thickness of just several

monolayers have become easier to achieve. For instance, wetting layers, such as copper and MoS₂, have been utilized to reduce the percolation threshold of noble metals and produce continuous films down to a few nanometers[58], [60], [65], [66]. Other techniques to obtain atomically smooth metal films involve e-beam evaporation of silver onto substrates cooled down to cryogenic temperatures to achieve high quality epitaxial plasmonic films[47], [67].

Epitaxial thin films are particularly beneficial in experimentally investigating the size dependent response of metals as there are no contributions to the optical properties from grain boundaries that would increase the scattering and losses. However, so far there have not been many demonstrations of epitaxial gold films down to thicknesses of just several monolayers. Additionally, while atomically thin epitaxial silver films with thicknesses of just 3 nm have been achieved[47], silver films are extremely chemically unstable and easily degrade when exposed to ambient environments, making it difficult to experimentally study the size dependent plasmonic behavior and realize practical devices with TD silver.

In contrast, titanium nitride (TiN) has been widely studied as an alternative plasmonic material due its chemical and mechanical stability, tailorability, and refractory properties. TiN has already been shown to have potential applications in photovoltaics[68], [69], waveguiding[7], [70], modulators[71], and nonlinear optical devices[51], [72]. Moreover, TiN can be grown epitaxially on lattice matched substrates such as c-sapphire and MgO, facilitating the development of ultra-thin, continuous films down to thicknesses of just 1 nm while maintaining a low roughness and high optical quality. Due to its high-quality growth, chemical and mechanical stability and tailorable optical properties, TiN is the ideal material choice to study the plasmonic properties as TDMs evolve from a few atomic layers to a bulk material. The electronic, optical and mechanical properties of TiN single or polycrystalline bulk system and thick films (>100 nm) have been largely studied[73]–[77] using several experimental and theoretical techniques, including spectroscopic ellipsometry[78], [79], X-ray, UV photoemission and Auger spectroscopy[80], [81], electron energy loss[82], [83], Hall electron transport[84], scanning electron and tunneling microscopies[85], [86], tight-binding and ab initio simulations[73], [87]–[89].

Although few reports on growth[90], [91] and electron transport[92], [93] of ultra-thin TiN films below thicknesses of 10 nm have appeared in the previous years, the optical properties

of TiN films in this thickness range are still largely underexplored. In this thesis, I will present our experimental and theoretical investigations on studying the thickness dependent optical properties of TiN in the TD regime. We experimentally demonstrate that TiN films with thicknesses down to 1 nm remain plasmonic in the visible and NIR wavelength range. Moreover, we use density functional theory (DFT) and a nonlocal Drude response model to theoretically explain the experimental thickness dependent trends observed, which are induced by strong electron confinement in the ultra-thin films. Finally, we explore the possibility of electrically tuning the properties as well as the ultrafast carrier dynamics in TD TiN.

1.6 Outline

This thesis contains the major results from our investigations on the evolution of the optical and plasmonic properties in transdimensional TiN.

Chapter 2 covers our initial studies on the plasmonic properties of unpassivated ultra-thin TiN with thicknesses down to 2 nm. We find a strong dependence of the optical response on the thickness, which is attributed to surface oxidation, increase in surface scattering, and quantum confinement effects. Despite the decreasing metallicity in thinner films, the thinnest films (2 nm) remain highly metallic with a high carrier concentration on the order of 10^{22} cm^{-3} .

Chapter 3 discusses our results from a joint experimental and theoretical investigation of the electrical and optical properties of ultra-thin TiN to understand the underlying physics that result in their thickness dependent properties. Using density functional theory (DFT) calculations, we reveal that the electron confinement in thinner films causing a redshift in the plasmonic response. We demonstrate that in this TD thickness regime, the thickness, surface oxidation, and substrate properties are crucial factors in controlling the optical behavior.

Chapter 4 introduces a nonlocal Drude response model that describes the confinement induced optical properties in plasmonic TD films. We characterize the optical properties of passivated TD TiN films with thicknesses ranging from 1-10 nm to verify the developed non-

local theory. Our experimental results demonstrate quantum confinement induced thickness dependent optical properties in plasmonic TD TiN.

Chapter 5 discusses the feasibility of electrically tuning the properties of atomically thin TiN. We demonstrate active control of the carrier concentration of a 1 nm TiN thin film. Based on the theoretically achievable carrier concentration modulation, a phase modulator is designed.

2. OPTICAL PROPERTIES OF ULTRA-THIN TITANIUM NITRIDE

Most of the content presented in this chapter is taken verbatim from the paper D. Shah, H. Reddy, N. Kinsey, V. M. Shalaev, and A. Boltasseva, “Optical Properties of Plasmonic Ultrathin TiN Films,” *Adv. Optical Mater.* 5 (13), 2017.

2.1 Introduction

With the continuing developments in nanofabrication techniques, structural dimensions and film thicknesses have been decreasing, which has led researchers to probe and understand light-matter interactions at the nanoscale. As the thickness of films approach just a few monolayers, the strong confinement could lead to quantum effects[94], [95] that could greatly enhance light-matter interactions[39], [96]. In addition, these films are expected to be more sensitive to external electrical[33] and optical perturbations, making them an attractive material platform for realizing dynamic nanophotonic and plasmonic applications. However, a key to realizing these applications is the ability to produce metallic films that are only a few monolayers in thickness, which also exhibit good optical and plasmonic properties.

For conventional plasmonic metals, such as silver and gold, continuous, smooth films with thicknesses lower than 10 nm are challenging to produce because of island formation and large defect concentrations which result from their high surface energy[60], [63], [97]. On the other hand, TiN, can be grown epitaxially on substrates such as c-sapphire and MgO, enabling the formation of continuous, plasmonic, ultra-thin films down to 2 nm[98], [99]. TiN has already been shown to have potential applications in photovoltaics[68], [69], waveguiding[7], [70], modulators[71], and nonlinear optical devices[51], [72]. Although some of these devices use films of 10 nm, there is an increasing interest in the formation of ultrathin metallic films (<10 nm) which may facilitate additional applications resulting from the strong confinement[30], nonlocal effects[40], and highly sensitive optical response[33] that arise in atomically thin films. To support this, there have been efforts to grow ultrathin TiN films using atomic layer deposition (ALD). However, these films become dielectric below 5 nm and may not be useful for nanophotonic applications[62]. This is because TiN thin films grown

using ALD with a TiCl_4 precursor are more prone to Cl impurities, which could result in a degradation of the metallic properties in thinner films[100]–[102].

In the present study, we have grown continuous, epitaxial, ultrathin TiN films that remain plasmonic in the optical range via DC reactive magnetron sputtering. Using sputtering to grow the film decreases the chance of contamination since only Ti, N, and Ar are introduced into the system, which helps maintain the metallic properties in ultrathin films. The complex dielectric permittivity of these films was characterized using spectroscopic ellipsometry, while charge carrier densities extracted from Hall measurements give further insight into the thickness dependent optical behavior of the films.

2.2 Methods

2.2.1 Material Growth

Ultra-thin TiN films with thicknesses of 2, 4, 6, 8, and 10 nm were grown on MgO using DC reactive magnetron sputtering. Due to the lattice matching between TiN and substrates such as MgO and sapphire, high quality, epitaxial films are possible and have been demonstrated using a similar growth technique in past studies[70], [99]. The TiN films were deposited by sputtering a titanium target in a 60% nitrogen and 40% argon environment at 5 mT with 200 W of DC power with the substrate heated to 800° C. A growth rate of 2.2 ± 0.1 nm/min was determined by depositing an approximately 200 nm thick sample over a fixed deposition time of 100 minutes and then measuring its thickness via SEM, which had a 5% error bar. Subsequently, the sputtering time for the desired thickness was calculated and films of desired thicknesses were grown. This growth procedure resulted in high quality, continuous films with low roughness of <0.21 nm, as shown in the atomic force microscopy (AFM) images of the 2 nm, 6 nm, and 8 nm films in Figure 2.1.

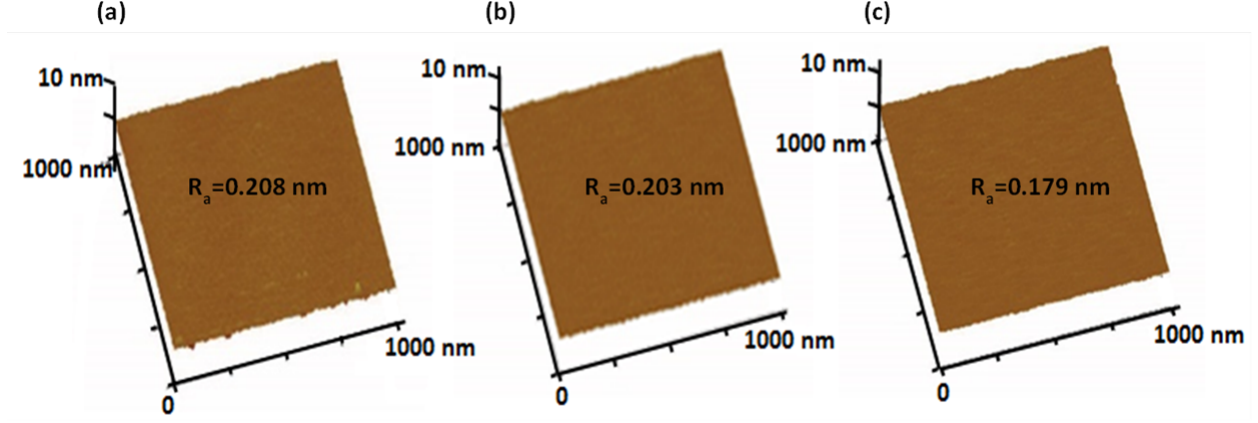


Figure 2.1. AFM images of (a) 2 nm, (b) 6 nm, and (c) 8 nm TiN films showing a very low roughness of <0.21 nm, indicating atomically smooth films

2.2.2 Optical Characterization

Ellipsometry measures the change in polarization of the reflected light from the sample's surface. This change is measured in terms of the amplitude ratio, Ψ , and the phase difference Δ ,

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)e^{i\Delta} \quad (2.1)$$

where R_p and R_s are the Fresnel reflection coefficients for p-polarized and s-polarized light respectively. The linear optical properties were measured using variable angle spectroscopic ellipsometry at angles of 50° and 70° for wavelengths from 400 nm to 2000 nm. The measured Ψ and Δ values at 50° and 70° are plotted in Figure 2.2.

The optical constants of TiN were determined by fitting the measured ellipsometry data using a Drude – Lorentz model,

$$\varepsilon(\omega) = \varepsilon_b - \frac{\omega_{pD}^2}{\omega^2 + i\Gamma_D\omega} + \sum_L \frac{f_L\omega_L^2}{\omega_L^2 - \omega^2 - i\Gamma_L\omega} \quad (2.2)$$

where ε_b is the high frequency background permittivity, ω_{pD} is the Drude plasma frequency, Γ_D is the Drude damping due to inelastic electron scattering, f_L , ω_L , and Γ_L are the strength, resonant frequency and broadening of the Lorentz oscillator, respectively. The

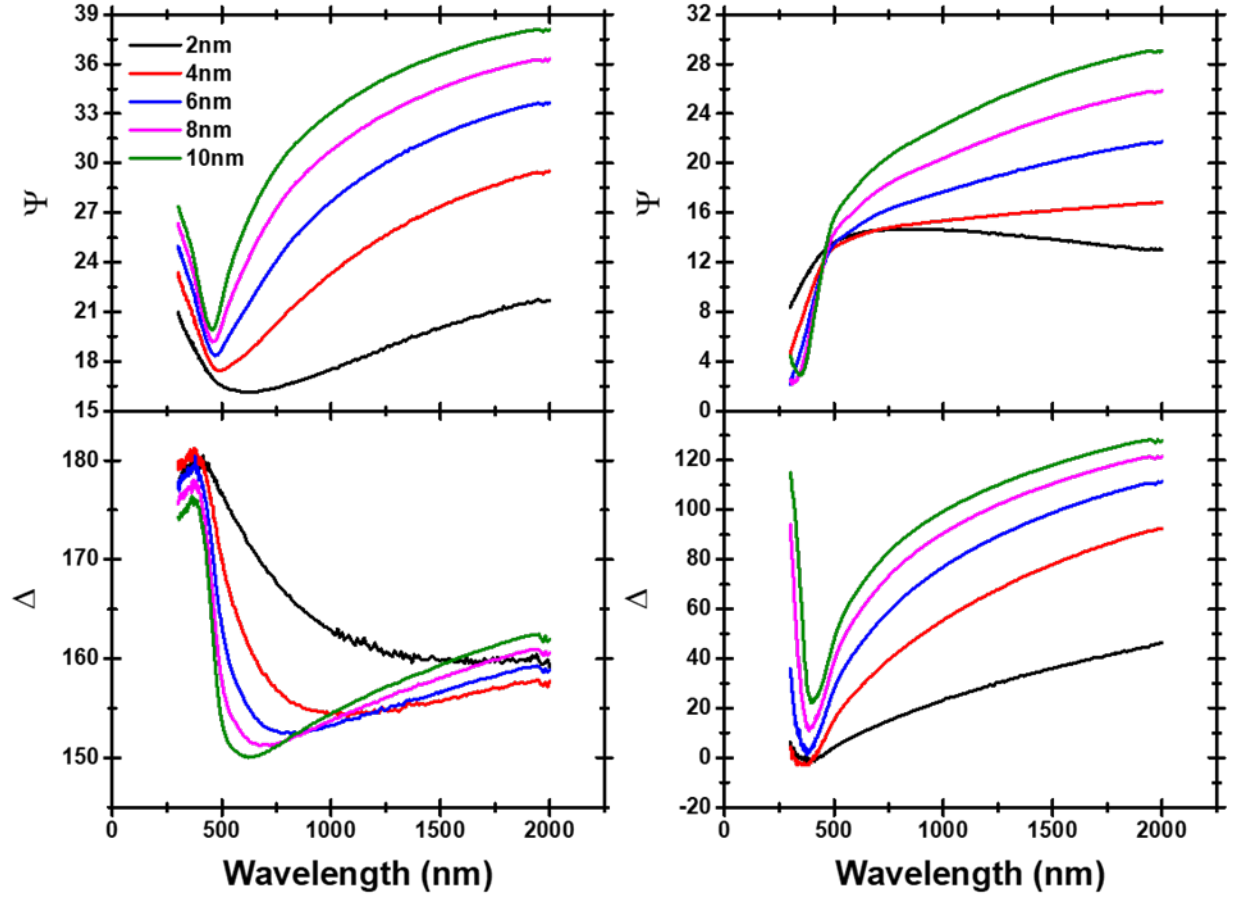


Figure 2.2. Ellipsometry measurements, Ψ and Δ , of the ultrathin films. (a) and (c) are Ψ and Δ for 50° , while (b) and (d) are Ψ and Δ for 70°

Drude term captures the optical response of the free carriers, while the Lorentz term accounts for interband transitions.

The real (ϵ') and imaginary (ϵ'') parts of the Drude oscillator in the complex dielectric permittivity in Eqn. (2.1) can be written as,

$$\epsilon'(\omega) = \epsilon_b - \frac{\omega_{pD}^2}{\omega^2 + \Gamma_D^2} \quad (2.3)$$

$$\epsilon''(\omega) = \frac{\omega_{pD}^2 \Gamma_D}{\omega^2 (\omega^2 + \Gamma_D^2)} \quad (2.4)$$

The Drude plasma frequency ω_{pD} is given by

$$\omega_{pD} = \sqrt{\frac{Ne^2}{m^*m_e\varepsilon_0}} \quad (2.5)$$

where N is the charge carrier density, ε_0 is the permittivity of free space, m_e is the mass of an electron, and m^* is the electron effective mass. The real part of the complex permittivity represents the strength of the polarization induced by an external electric field. It also signifies how metallic the plasmonic film since it is proportional to the charge carrier density through the Drude plasma frequency. The imaginary part of the complex permittivity describes the optical losses encountered in the material.

In atomically thin films, the strong confinement in thickness leads to the emergence of quantum phenomena, which may not be accurately captured by a simple Drude-Lorentz model. However, the thinnest film considered in the current study (2 nm) is nearly five monolayers in thickness. A recent computational work on atomically thin gold films[33] revealed that the optical properties described by a simple classical free electron model match well with quantum mechanical calculations. It is therefore reasonable to describe the dielectric function of all the presented films with a Drude-Lorentz model, given that they are several monolayers in thickness. For even thinner films, quantum size effects may lead to deviations in the Drude-Lorentz model, but these studies are beyond the scope of current work.

2.2.3 Electrical Characterization

The carrier densities in the TiN films were measured using standard Hall measurements. Using photolithography and a dry etching process, Greek crosses were fabricated from the TiN films and gold contact pads were applied. Positive resist AZ-1518 was spin coated onto ultrathin TiN films at 4000 rpm. The coated samples were then soft baked at 100 °C for 55 s. Subsequently, the Greek crosses were patterned using the Karl Suss MJB3 Mask Aligner and developed in MF 26A for 40 sec. The developed samples were then dry etched (Panasonic E620) using an optimized chlorine etch recipe, producing the Greek crosses. Finally, 180 nm thick gold contact pads were deposited using a lift-off technique. A 6 nm Ti layer was used

as an adhesive layer during deposition. Hall measurements of planar materials are more susceptible to error due to a finite contact size. Subsequently, the influence of the finite contacts on the measurements can be mitigated by using a Greek cross geometry (Figure 2.3)[103]. Figure 2.3 shows an optical image of a fabricated Greek cross on an 8 nm TiN film. The Hall coefficient was determined by measuring the voltage across two arms of the cross while a current (10 mA) passing through the other two arms generates an out-of-plane magnetic field. Because the relationship between the Hall resistance R_H and the applied magnetic field B is linear,

$$B = NdeR_H \quad (2.6)$$

where N is the carrier density and d is the thickness of the film, the carrier density N can be extracted.

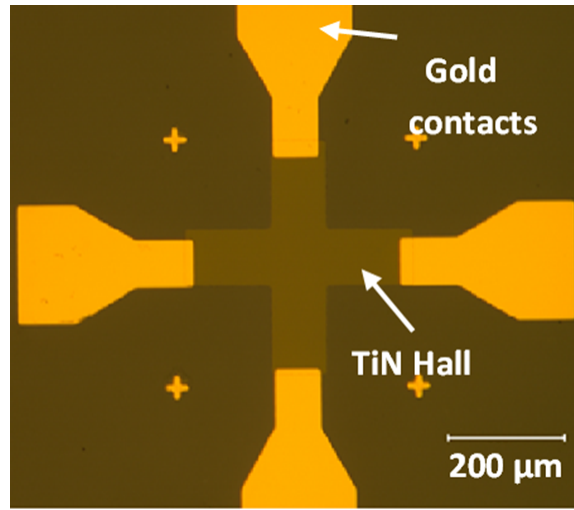


Figure 2.3. Optical image of the an 8 nm Hall cross with the gold contact pads used for extracting the charge carrier densities. The Hall cross was fabricated using photolithography and a dry etching process.

2.3 Results

2.3.1 Optical Properties of Ultrathin TiN

The Drude – Lorentz model parameters that describe the complex dielectric permittivity per Eqn. 2.2 are given in Table 2.1, and the real and imaginary parts are plotted in Figure 2.4a and 2.4b, respectively. As the thickness decreases, the films are observed to become less metallic as signified by the decrease in the magnitude of the real part of the dielectric permittivity. This is consistent with the results from the Hall measurements (Figure 2.5) which show that the free electron concentration decreases along with film thickness. The decreasing carrier concentration can be attributed to an increase in the films’ defect concentration caused by the presence of a 2 nm layer of TiN_xO_y that is typically formed on the surface of TiN films[104], [105]. In thinner films, due to a larger surface to volume ratio, the relative oxygen concentration increases, resulting in a reduced free carrier density. However, we note that the thinnest films (2 nm) still have a carrier density on the order of 10^{22} cm^{-3} , demonstrating that they retain their metallic character.

Table 2.1. Ellipsometry fitting parameters for ultra-thin TiN using a Drude - Lorentz model

Thickness (nm)	2	4	6	8	10
ε_{inf}	0.92	2.66	2.95	3.11	3.28
$\omega_{pD}^2 \text{ (eV}^2\text{)}$	34.98	44.97	48.2	50.2	51.66
$\Gamma_D \text{ (eV)}$	0.282	0.247	0.236	0.232	0.229
$f_1\omega_1^2 \text{ (eV}^2\text{)}$	0.28	0.58	0.7	0.68	0.72
$\Gamma_1 \text{ (eV)}$	0.35	0.45	0.5	0.49	0.53
$\omega_1 \text{ (eV)}$	2.15	2.16	2.18	2.19	2.16
$f_2\omega_2^2 \text{ (eV}^2\text{)}$	113.9	105.2	100.1	99.6	96.7
$\Gamma_2 \text{ (eV)}$	2.38	2.48	2.47	2.54	2.53
$\omega_2 \text{ (eV)}$	4.44	4.65	4.7	4.78	4.79

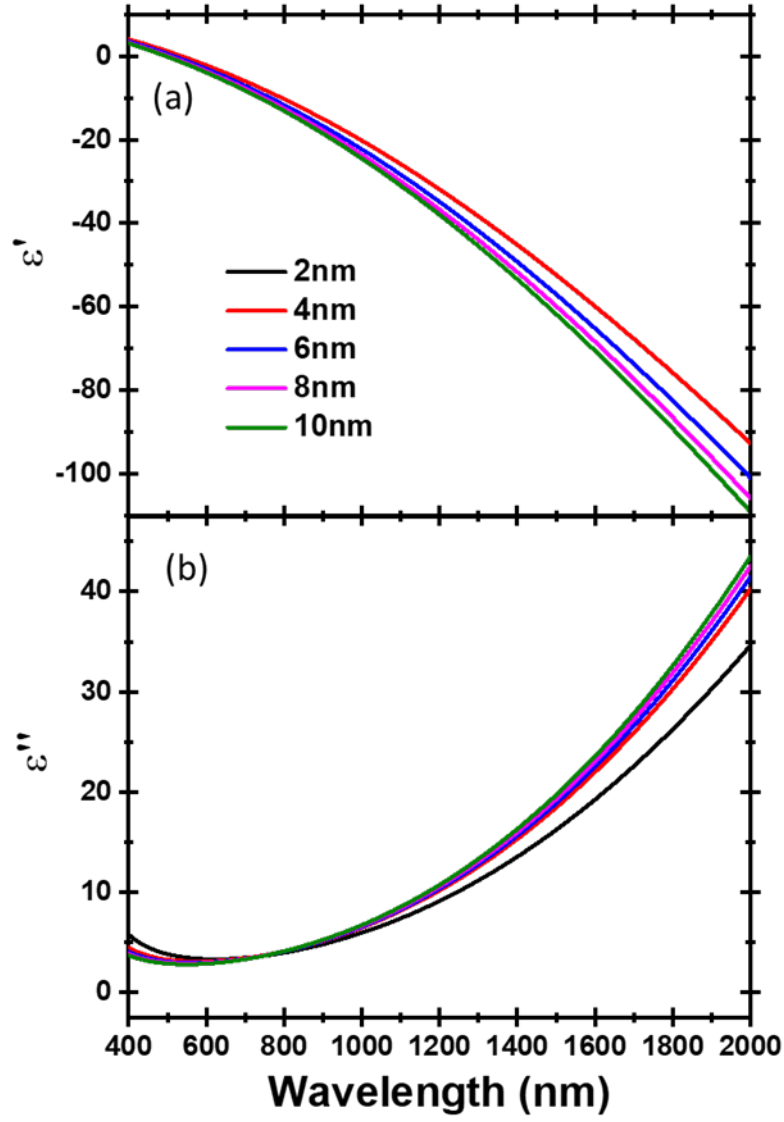


Figure 2.4. Thickness dependent (a) real and (b) imaginary parts of the dielectric permittivity as retrieved from ellipsometry measurements. The films become less metallic with decreasing thickness.

Additionally, at visible wavelengths, we see an increase in the imaginary part of the permittivity of thinner films, while there is a decrease in thinner films in the near infrared. According to Eqn. 2.4, ϵ'' is quadratically proportional to the Drude plasma frequency and linearly proportional to the Drude damping. In order to understand the experimental trends for ϵ'' , I will first discuss the thickness dependent trends of the Drude damping and plasma frequency that were retrieved from the ellipsometry fittings.

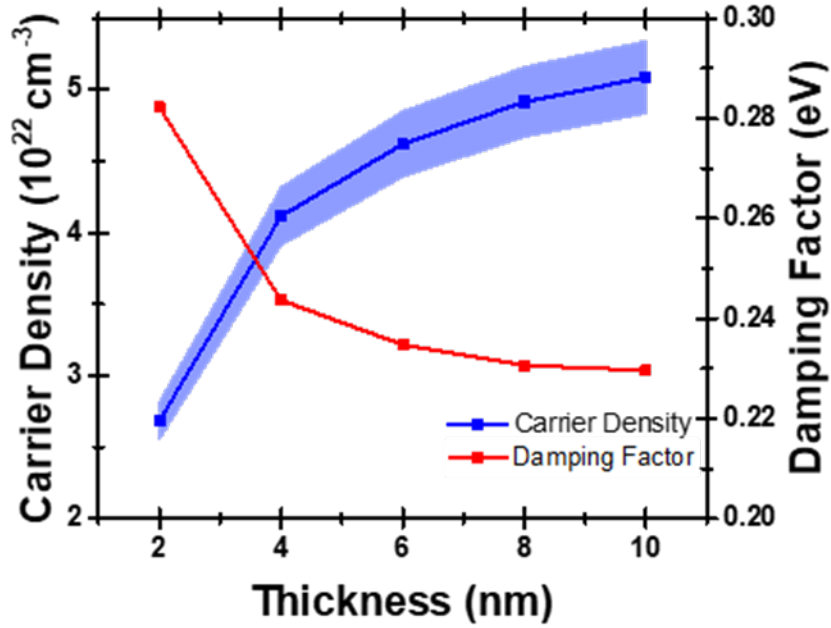


Figure 2.5. Carrier densities obtained from Hall measurements and damping factor from ellipsometry measurements. As the thickness decreases, the metallic character decreases and the scattering losses increase. The error bar for the carrier densities is obtained from the error in the sputtering rate.

2.3.2 Scattering Losses in Ultrathin TiN

Additionally, in Fig. 2.5 we see an increase in the Drude damping factor for thinner films, as obtained from ellipsometry. In general, there are five scattering processes which produce the losses in thin films, which include bulk scattering due to thermal lattice vibrations, electron-electron scattering, surface scattering, defect scattering, and grain boundary

scattering. Since the films are epitaxial, scattering at grain boundaries can be neglected. On the other hand, as the film thickness decreases, both defect and surface scattering become important contributors to losses[106]. When the film thickness is reduced below the mean free path of the bulk material, the surface scattering increases as[107]

$$\frac{1}{\tau_{ss}} = \frac{5Ne\rho_b\lambda}{8m^*m_e d}(1-p) \quad (2.7)$$

where N is the carrier concentration, e is the electron charge, m^* is the effective mass, m_e is the electron mass, ρ_b is the bulk resistivity, λ is the electron mean free path, d is the film thickness, and p is a scattering parameter. The scattering parameter, p , may vary from 1 for complete specular scattering to 0 for complete diffuse scattering. For the case of bulk titanium nitride, the mean free path is approximately 45 nm[92], which is considerably greater than the film thicknesses studied such that surface scattering is expected to be significant. Additionally, the defect concentration is expected to increase for thinner films. Since the oxygen defects are primarily located within 2 nm from the surface, a reduction in the thickness results in a higher overall density of defects and subsequently an increased scattering probability.

2.3.3 Thickness Dependent Drude Plasma Frequency

The plasma frequency, ω_{pD} , of each film as extracted from the fitted ellipsometry models (with the error ranging from 2% to 8%) is also observed to decrease with film thicknesses as plotted in Figure 2.6. The plasma frequency is dependent on the carrier concentration and the effective mass of the electrons by the definition

$$\omega_{pD} = \sqrt{\frac{Ne^2}{m^*m_e\varepsilon_0}} \quad (2.8)$$

where N is the charge carrier density, ε_0 is the permittivity of free space, m_e is the mass of an electron, and m^* is the electron effective mass. Since the plasma frequency is proportional to the square root of the carrier concentration, ω_{pD} gives a gauge for the metallic character of the films. Consequently, changes in the plasma frequency can be attributed to either the

carrier density, which is observed to decrease with thickness in our films, or the electron effective mass.

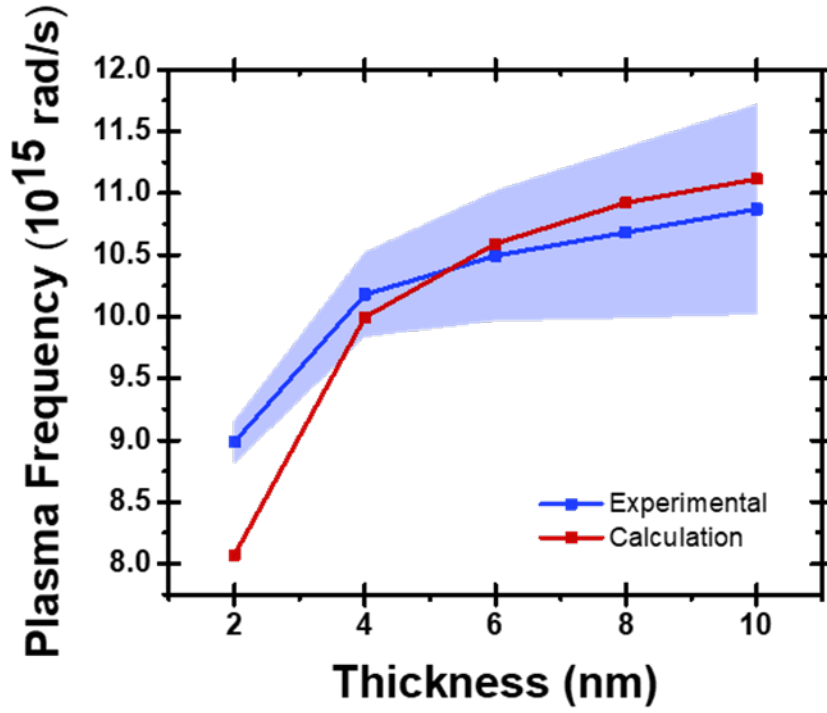


Figure 2.6. Plasma frequency extracted from the ellipsometry fittings (blue) compared to the plasma frequency calculated assuming an average effective mass (red). Below 4 nm, the calculated plasma frequency is outside of the error bar for the ellipsometry values and begins to deviate from the experimental trend, which may be a result of either modifications in the band structure caused by the oxynitride or quantum confinement effects.

2.3.4 Thickness Dependent ϵ''

As mentioned earlier, ϵ'' increases in thinner films in the visible range, while it decreases in thinner films in the near infrared. This can be understood from the experimental trends observed for the Drude damping and Drude plasma frequency, since ϵ'' is dependent on both of these parameters. We experimentally observe a decrease in the plasma frequency and an increase in the damping factor as the thickness decreases. Both of these trends would have an opposing effect on the thickness dependent ϵ'' , since the plasma frequency would result in a decrease in the overall response while the damping factor would cause an increase. At

longer wavelengths in the near infrared, we find that the thickness dependent trend of the plasma frequency dominates over the damping factor the resulting optical behavior as ε'' begins to decrease in the thinner films.

2.3.5 Role of Effective Mass in the Thickness Dependent Optical Properties

From Equation 4, the electron effective mass is calculated using the values of ω_{pD} from the ellipsometry and the carrier concentration from the Hall measurements. Subsequently, the effective mass is also found to decrease along with the film thickness, as seen in Figure 4b. However, this trend in the effective mass would produce an increasing trend in the plasma frequency. Consequently, we conclude that the reduction of the carrier concentration dominates the effect on the plasma frequency, resulting in the reduced plasma frequency for thinner films. To assess the significance of the effective mass on the optical properties, the square of the plasma frequency is plotted as a function of the carrier concentration in Figure 4c. In this case, ω_{pD}^2 is linearly proportional to the carrier concentration, implying that in comparison to the carrier concentration, the effective mass is relatively constant. Based on a linear fit of the plot in Figure 4c, an average effective mass of 1.31 is determined. Using this average effective mass, the plasma frequency is then calculated using Equation 4 and the carrier concentrations from the Hall measurements and replotted in Figure 2.6. For film thicknesses of 4 nm to 10 nm, the calculated plasma frequency falls within the error bar of the experimental values. However, below 4 nm, the model begins to breakdown, and we see a deviation from the experimental values for the 2 nm film. In this case, when the thickness is decreased to 2 nm, we expect a predominantly TiN_xO_y material. Consequently, the oxygen defects in the film may produce strain in the film which modifies the conduction band curvature and hence, the effective mass. Additionally, quantum confinement may arise in films with thicknesses less than 10 nm, as they do in semiconductor quantum wells, and may also lead to modification of the effective mass. Such effects may also explain the deviation in the optical properties experienced for thicknesses below 4 nm [108], [109] although further investigations are required to quantify the role quantum effects play in ultrathin TiN films. Furthermore, the small lattice mismatch between MgO (4.21 Å) and

TiN (4.24 Å) invariably introduces strain into the TiN films which would result in a modified effective mass. However, with increasing thickness, the internal strain slowly fades away and the band structure approaches that of bulk. Based on our experimental findings, we conclude that the threshold thickness below which the band structure begins to deviate due to these effects to be 4 nm.

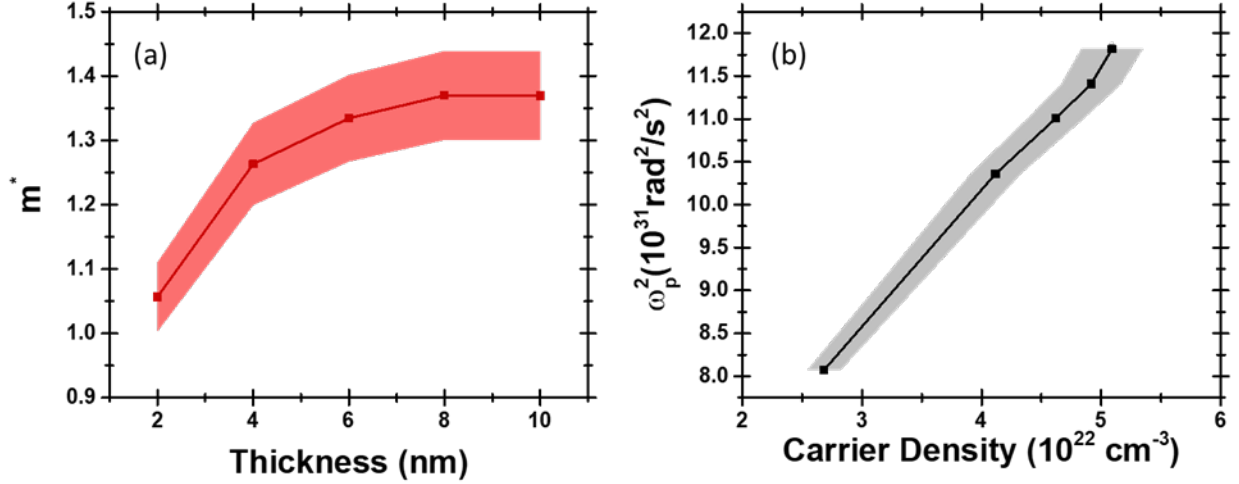


Figure 2.7. (a) Calculated effective mass using Hall measurements and ellipsometry results. (b) Plasma frequency squared as a function of carrier density, which is observed to be linearly proportional, indicating that the effective mass may be relatively constant. The slope of (b) is used to calculate the average effective mass.

2.3.6 Thickness Dependent Resistivity

The resistivity measured from the optical and electrical characterizations are compared. The optical resistivity of the films is calculated using the Drude damping factor and plasma frequency obtained from the ellipsometry fittings, as

$$\rho = \frac{\Gamma_D}{\varepsilon_0 \omega_{pD}^2} \quad (2.9)$$

The electrical resistivity is measured using the four-point probe method on the ultra-thin films. The resistivity from both electrical and optical measurements are plotted in Figure 2.8.

For both the electrical and optical measurements, the resistivity increases in thinner films and qualitatively follow a similar trend as each other. In the case of the calculations based on the optical measurements, the increase in the Drude damping and the decrease in the plasma frequency for thinner films both contribute to a higher resistivity. The increase in resistivity for both optical and electrical measurements can be explained by the increase in scattering events caused by more surface and defect scattering as well as a decrease in the carrier concentration in thinner films.

Differences in the measured data may be attributed to how the scattering effects contribute to the resistivity calculations in each technique. In ellipsometry, the scattering originates from the electrons' interaction with light. On the other hand, electrical measurements depend on the scattering during the electron's path from one electrode to another.

2.4 Summary

Overcoming the challenge of growing high quality, continuous ultra-thin films that remain metallic is of great importance for practical applications of plasmonic structures. We have developed deposition techniques to grow epitaxial quality, ultra-thin TiN films (<10 nm) with low roughness using DC magnetron sputtering. Using spectroscopic ellipsometry and Hall measurements, we have investigated their optical and electrical properties. Metallic properties are retained in films with thicknesses as low as 2 nm, which exhibit a high carrier concentration and remain plasmonic in the visible and near infrared wavelength range. We observed that with reduced thickness the films become less metallic and more lossy, which is explained by a decrease in the carrier concentration as well as larger number of scattering events caused by higher surface and defect scattering. Based on the relationship between the plasma frequency, carrier concentration, and effective mass, it is determined that the reduction in carrier concentration plays the main role in defining the film's optical properties,

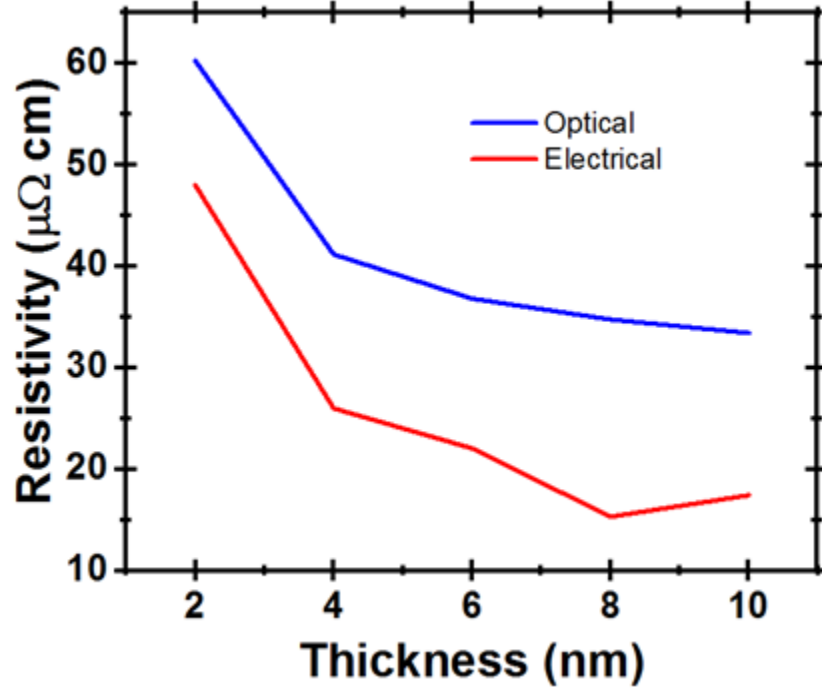


Figure 2.8. Optical and electrical resistivity retrieved from ellipsometry and four-point probe measurements, respectively. Increases in the resistivity is due to the lower carrier concentration due to oxidation and a higher losses due to more surface scattering in thinner films as a result of Differences in the calculated resistivity is due to the different scattering effects that contribute to each technique.

as variations in the effective mass are found to be minimal for thicknesses above 4 nm. For the 2 nm film and below, theoretical calculations begin to deviate from experimental values.

3. FIRST PRINCIPLE STUDIES OF ULTRATHIN TITANIUM NITRIDE

Most of the content presented in this chapter is taken verbatim from the paper D. Shah, A. Catellani, H. Reddy, N. Kinsey, V. M. Shalae, A. Boltasseva, and A. Calzolari, "Controlling the Plasmonic Properties of Ultrathin TiN Films at the Atomic Level," ACS Photonics 5 (7), 2018.

3.1 Introduction

While we've experimentally demonstrated the retention of high metallicity and changes in the optical properties in ultra-thin TiN films[41], a comprehensive investigation of the underlying physics affecting the plasmonic properties in ultra-thin metal films is mandatory to devise processes and control the film properties. Hence, to move towards the realization of practical devices utilizing ultrathin plasmonic materials, additional studies are required to understand the optical behavior of ultrathin films and the different factors contributing to their thickness dependent properties. In this chapter, we present a joint theoretical-experimental study on the plasmonic properties of ultra-thin TiN films. We have conducted a detailed theoretical and experimental study on the plasmonic behavior of ultrathin (down to a few atomic layers) TiN films to determine the role of thickness, surface oxidation and interface strain on TiN optical properties. Structural and compositional characterization of the films provide further insight into the possible avenues to tailor the optical response. We show that the effects of oxidation and strain on the optoelectronic and plasmonic properties of the thin films emerge as fundamental parameters to optimize the nanostructure response.

3.2 Methods

3.2.1 Density Functional Theory (DFT)

First principles density functional (DFT) calculations are carried out with semilocal (PBE[110]) exchange-correlation functional, using plane wave basis set (with a cutoff energy of 200 Ry) and norm-converging pseudopotentials[111], as implemented in Quantum

Espresso[112] codes. A uniform (28x28) k-point grid is used for summations over the 2D Brillouin zone.

Extended TiN films are simulated using periodically repeated supercells. Each unit cell $(4.24 \times 4.24 \times 55.00) \text{ \AA}^3$ has a $(\sqrt{2} \times \sqrt{2})$ 2D lateral periodicity and contains 1 to 10, 15 and 20 layers of TiN(001), as shown in Figure 1a. The lattice parameter of TiN surface (4.24 Å) is obtained from the optimization of the corresponding bulk crystal[90]. When considering the effect of oxidation, O adatoms are symmetrically adsorbed on each surface to avoid a spurious dipolar field across the cell. To avoid interaction between adjacent slab replicas, these are separated by at least 15.0 Å of vacuum. Each structure is fully relaxed until forces on all atoms become lower than 0.03 eV/Å.

The complex dielectric function $\varepsilon = \varepsilon' + i\varepsilon''$ is evaluated using the code epsilon.x, also included in the Quantum ESPRESSO suite. This code implements an independent particle formulation of the frequency-dependent (ω) Drude–Lorentz model for solids[111], [113]:

$$\hat{\varepsilon}(\omega) = \varepsilon' + i\varepsilon'' = 1 - \sum_{\mathbf{k},n} f_{\mathbf{k}}^{n,n} \frac{\omega_p^2}{\omega^2 + i\eta\omega} + \sum_{\mathbf{k},n \neq n'} f_{\mathbf{k}}^{n,n'} \frac{\omega_p^2}{\omega_{\mathbf{k},n,n'}^2 - \omega^2 - i\gamma\omega} \quad (3.1)$$

where $\omega_p = \sqrt{\frac{e^2 n_e}{m^* \varepsilon_0}}$ is the bulk plasma frequency, e is the electron charge, n_e the electron density, ε_0 the dielectric permittivity of vacuum and m^* the electron effective mass. $\hbar\omega_{\mathbf{k},n,n'} = E_{\mathbf{k},n} - E_{\mathbf{k},n'}$ are the vertical band-to-band transition energies between occupied and empty Bloch states, labelled by the quantum numbers $(\mathbf{k}, n)$ and $(\mathbf{k}, n')$, respectively. $f_{\mathbf{k}}^{n,n}$ and $f_{\mathbf{k}}^{n,n'}$ are the oscillator strengths for the Drude and Lorentz parts and are related to the dipole matrix elements between Bloch states. η and γ are the Drude-like and Lorentz-like relaxation terms, which account for the finite lifetime of the electronic excitations and implicitly include the effects of the dissipative scattering. The capability of the present approach in simulating the optical properties of plasmonic materials has been extensively proved in Refs.[89], [113], [114]. As a further accuracy test, we report in the Supporting Information (SI) the comparison between the dielectric function of TiN bulk (B1 phase) calculated with Drude-Lorentz approach and with the one based on Time-Dependent Density Functional Perturbation Theory, adopted in Ref [89].

The free carrier density n_e is obtained inverting the Drude-like expression for the plasma frequency, $n_e = (\omega_p^2 \epsilon_0 m^*) / e^2$. Rigorously, since TiN has a non-spherical Fermi surface with three bands crossing the Fermi energy, m^* is direction and band dependent. On the other hand, it is an experimental custom to assume a single parabolic model and extract an average m^* (usually deriving from optical measurements) to combine it with resistivity measurements in order to estimate the experimental carrier density. For bulk systems the estimated m^* is very close to the free electron mass m_0 ($m^* = 1.1m_0$)[84]. For films thicker than 2 nm the average effective mass is about $1.3m_0$ and it is expected to decrease for thinner films[61]. Direct evaluation from our DFT band structure calculation around Γ point gives $m^* = 0.99m_0$ for bulk and $m^* = 0.9m_0$ for 4L film, respectively, in good agreement with experimental estimates. In the following, for the calculation of n_e we assumed $m^* = m_0$ for each system, with an error band (orange shaded area, Figure 1) among the extrema $m^* = 0.9 - 1.3m_0$.

3.2.2 Material Growth

Ultrathin TiN films with thicknesses of 2, 4, 30, and 100 nm were grown on MgO using DC reactive magnetron sputtering. The TiN deposition was completed by sputter deposition of a titanium target in a 60% nitrogen and 40% argon environment at 5 mT with 200 W of DC power with the substrate heated to a temperature of 800° C, resulting in high quality epitaxial films with low roughness[61].

3.2.3 X-ray Photoelectron Spectroscopy

The Kratos X-ray photoelectron spectrometer was used for the surface analysis of a 30 nm TiN film. A monochromatic Al K- α (1486.6 eV) X-ray source was used as the incident radiation. The wide scan for the overall spectra is performed with a scanning step of 1000 meV, while the narrow scans for the elemental peaks are performed with a scanning steps of 50 meV. The narrow scans were peak fitted using the CasaXPS software. The spectral energy scale was calibrated with the binding energy of C 1s set to 284.5 eV.

3.2.4 Optical Characterization

The linear optical properties of the 2, 4, and 100 nm films were measured using variable angle spectroscopic ellipsometry at angles of 50° and 70° for wavelengths from 400 nm to 2000 nm. A Drude-Lorentz model consisting of one Drude oscillator and one Lorentz oscillator was used to fit the measurements.

3.3 Results and Discussion

3.3.1 DFT Modelling of the Electrical and Optical Properties of Ultrathin TiN

The electrical and optical properties of ultrathin TiN with thicknesses ranging from one to twenty monolayers (0-4 nm) calculated using DFT are summarized in Figures 3.1 and 3.2. Figure 3.1b) reports the thickness variation of the free electron density n_e . Figure 3.1c) displays the thickness variation of the volume-plasmon energy $E_p = E(\omega_p)$ and of the screened-plasmon energy $E_0 = E(\omega_0)$, where $\omega_0 = 2\pi c/\lambda_0$, and λ_0 corresponds to the wavelength where the real part (ε') of the dielectric function changes sign ($\varepsilon'(\lambda_0) = 0$). Figure 3.2 shows the plots of the (ε') function as resulting from the solution of Drude-Lorentz model of Eqn. (3.1).

All systems exhibit a metallic character and, except for the single layer (1L), have a high carrier density of the order of 10^{22} cm^{-3} , in agreement with the experimental results[61] that were presented in Chapter 2. Nonetheless, with decreasing thickness, the films become less metallic. The electron density n_e decays almost linearly with the number of layers NL (Figure 3.1b) and the real part of the dielectric function (Figure 3.2) decreases in magnitude as a function of NL (the imaginary part also decreases, not shown). The latter is an indication of the progressive reduction of the electronic screening in ultrathin layers. Additionally, the crossover wavelength λ_0 red shifts as the thickness decreases. This trend is in qualitative agreement with the experimental results summarized in Chapter 2, where the optical properties of epitaxial ultrathin TiN films with thicknesses of 2, 4, 6, 8, and 10 nm grown on MgO were measured using variable angle spectroscopic ellipsometry.

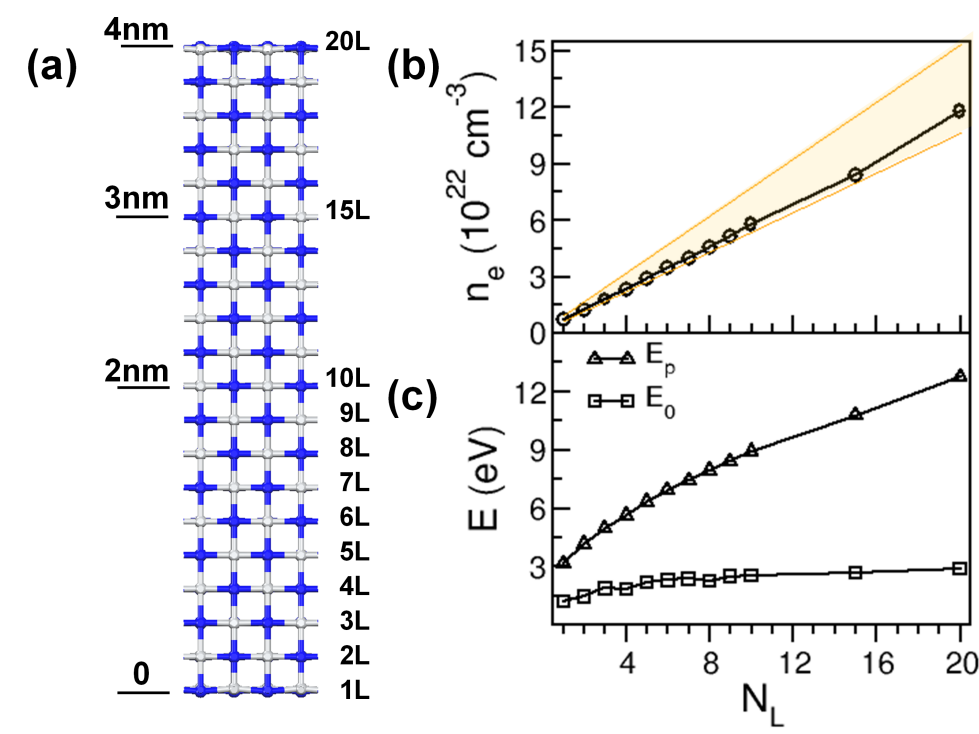


Figure 3.1. (a) Side view of 1-10, 15 and 20 layer thick TiN(100) slabs used in the simulations. (b) free electron charge density n_e , and (c) volume-plasmon E_p and screened-plasmon E_0 energies for 1-20 layer films. Although the 20 monolayer thick TiN is highly metallic, the bulk limit for the plasmon energies is not yet reached. The orange shaded area estimates the error bar associated with the choice of m^*

It is important to note that, although the theoretical results cover a smaller range of thicknesses (0-4 nm) and directly compare only with the two thinnest experimental samples (2-4 nm), they are still well representative of the trends showed by the experimental results. This is confirmed also by the $1/N_L$ fit of E_0 displayed in Figure 3.3. In order to extrapolate the limit for films of increasing thickness, we plot (Figure 3.3) the screened plasmon energy E_0 as a function of $1/N_L$, where N_L is the number of layers in the simulated system. Two distinct regimes are clearly evident: one dominated by quantum confinement effect for very thin films (1-3 layers, open red circle), one (filled circles) for thicker films. This indicates that trends from theoretical results are meaningful for comparison with experimental data even for thicker films. Figure 3.3 shows that, except for 1L-3L systems, all the other results

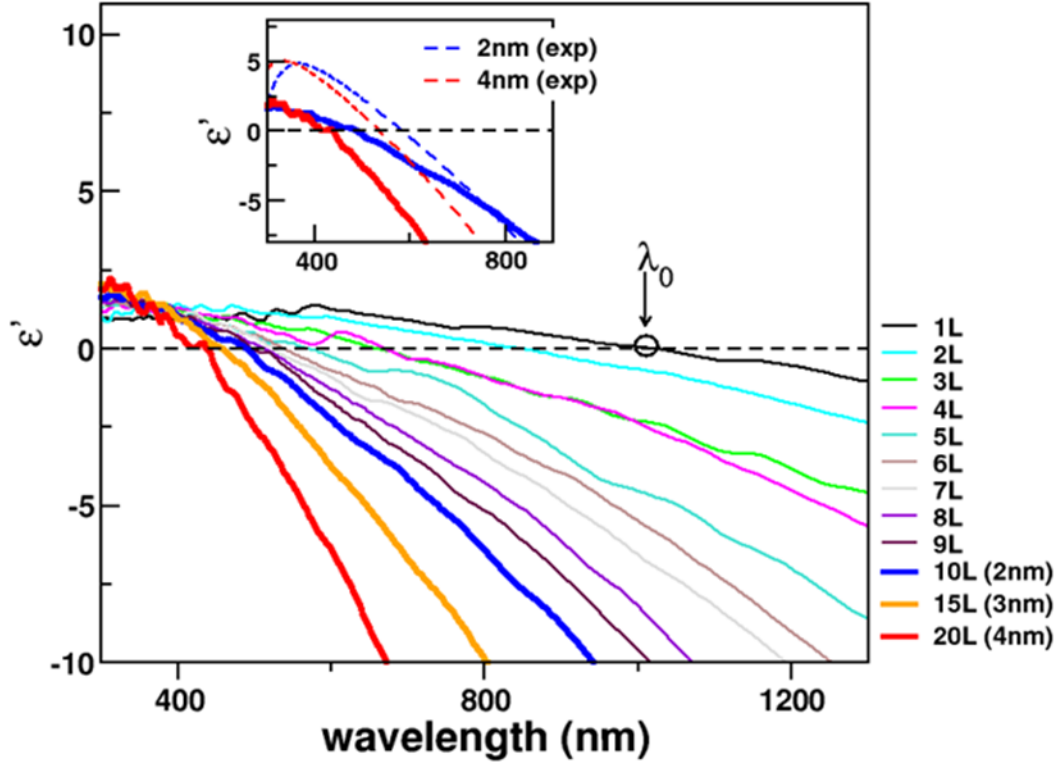


Figure 3.2. (a) Side view of 1-10, 15 and 20 layer thick TiN(100) slabs used in the simulations. (b) free electron charge density n_e , and (c) volume-plasmon E_p and screened-plasmon E_0 energies for 1-20 layer films. Although the 20 monolayer thick TiN is highly metallic, the bulk limit for the plasmon energies is not yet reached. The orange shaded area estimates the error bar associated with the choice of m^*

present a linear behavior as the number of layers ($1/N_L$) increases (decreases), and the trends can thus be used to compare with experimental data for thicker films.

At the crossover wavelength λ_0 , the imaginary part of the dielectric function ϵ'' also has a minimum. The condition $\hat{\epsilon}(\lambda_0) \approx 0$ corresponds to the possibility of exciting a plasmon-like resonance in the visible range[89], [115], [116]. The difference between E_p and E_0 for each thickness value (Figure 3.1c) indicates that the plasmon excitations in the optical range (E_0) do not involve the overall charge density of the system, as for the high energy volume plasmon (E_p), but only a reduced “screened” fraction ($n_e \approx 10^{21} \text{ cm}^{-3}$). This is the result of a complex interplay between interband and intraband transitions that effectively screen the amount of

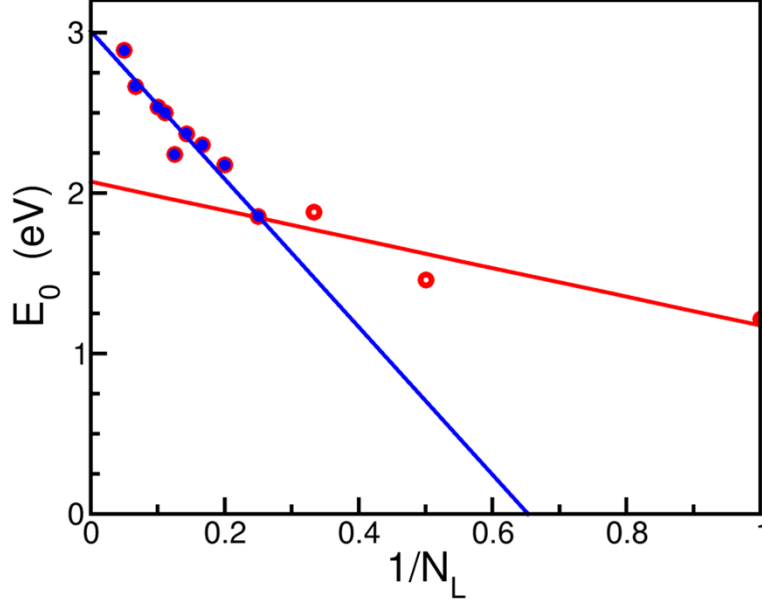


Figure 3.3. Screened plasmon energy E_0 as a function of the number of TiN(100) layers (N_L).

free charge that can be collectively excited in the optical range[90]. E_p and E_0 have two evident functional trends as a function of the thickness: E_p varies in the range 3.1-12.7 eV (1L-20L) with an almost ideal square root behavior (i.e. n_e varies linearly with thickness), while E_0 is limited to a much smaller variation range 1.2-2.9 eV for 1-20 layers, respectively, due to the interband-transition screening that is active even in ultrathin films (see below). We further note that the value of volume-plasmon for TiN bulk is $E_p^{bulk} = 25.4\text{eV}$ [82], [89], larger than the values resulting in the present case: Despite their metallic character, these films have not yet reached the bulk (or thick-film) density limit, remaining well within the ultrathin regime.

The red shift of the crossover wavelength along with the reduction of the real and imaginary parts of the dielectric function when the thickness is reduced perfectly fits with a recent electromagnetic model explicitly developed to describe the confinement effects on the optical properties of ultrathin plasmonic films[40]. Here, taking advantages of first principles results, we can discuss the effect of quantum confinement in terms of the electronic structure of the ultrathin films. The electron density of states (DOS) of each TiN film close to the Fermi

energy (E_F) is characterized by two contiguous groups of bands, labeled **1** and **2** in Figure 3.4, which shows the DOS spectra for the cases 1L (red) and 10L (black).

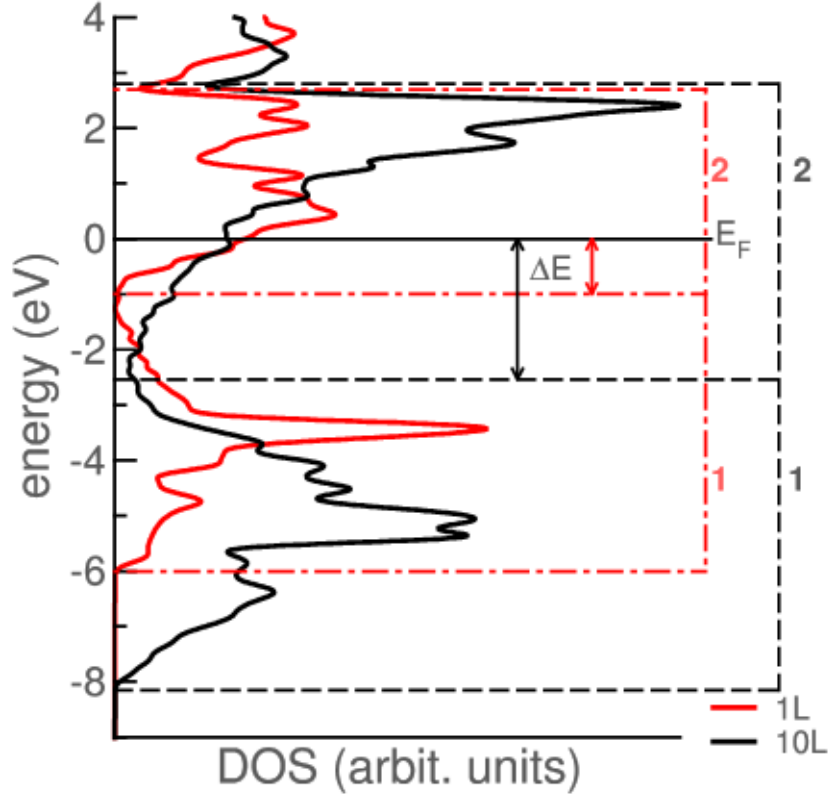


Figure 3.4. Simulated DOS plots for 1L (red) and 10L (black) systems. Dashed lines remark energy position with respect to the Fermi level (E_F) and the energy width of the two main groups of bands (1, 2) responsible for crossover wavelength in the visible range (λ_0). Due to electron confinement, a shrinking in the energy bandwidth is observed, resulting in the red shift of the crossover wavelength observed in Figure 3.2

Bands forming the multiplet **1** have a predominant N($2p$) character with a minor contribution from Ti(e_g) orbitals, while bands of group **2** mostly derive from Ti(t_{2g}) orbitals slightly hybridized with N($2p$) states. The plasmonic behavior of TiN originates from intraband transitions of group-2 bands that cross the Fermi level, giving rise to a Drude-like tail in the real part of the dielectric function and to the high-energy volume plasmon. The excitation of interband **1** $\rightarrow$ **2** transitions at lower energies gives a positive contribution to the (negative) Drude component of ϵ' that becomes globally positive at the crossover frequency λ_0 . Thus, in a first approximation, the energy position of band **1** with respect to the Fermi level (ΔE

in Figure 3.4) defines the energy of the screened plasmon (E_0). The effect of confinement actually changes the energy width and the energy position of bands 1 and 2 with respect to E_F . Despite the two sets of bands are clearly present in both systems, their characteristics are quite different: with decreasing thickness the surface-to-bulk ratio increases along with the number of under-coordinated surface atoms. The presence of frustrated bonds imparts a shrinking of the bandwidth of bands 1 and 2 (i.e. higher spatial electron localization), and an upshift of occupied bands (i.e. lower binding energies), which results in a decrease of ΔE (i.e. E_0 red-shifts). Thus, despite the same formal electron density, the reduction of thickness increases the surface contribution and the electron localization, giving an effective reduction of the free electron charges.

This qualitatively explains the modifications of the optical properties observed in the experiments varying the film thickness[61]. In order to have a more quantitative comparison, we superimpose the experimental ε' spectrum (inset of Figure 3.2) for the 2 nm and 4 nm films. Albeit in qualitative agreement, the theoretical values of λ_0 are systematically blue shifted with respect to the experimental ones, i.e. the crossover wavelength of 2 nm and 4 nm TiN films are reached at a larger thickness in the experimental studies compared to the theoretical results. In particular, the theoretical value of λ_0 for the 10L system (i.e. 2nm), $\lambda_0=489$ nm (blue straight line), is blue-shifted by 96 nm with respect to the experimental value, $\lambda_0=585$ nm (blue dashed line). For the 20L system (i.e. 4nm), $\lambda_0=430$ nm (red straight line), is blue-shifted by 105 nm with respect to the experimental value, $\lambda_0=535$ nm (red dashed line). Two different factors that may originate the λ_0 difference between experiment and theory are considered: (i) surface oxidation and (ii) interface strain.

3.3.2 Effect of Surface Oxidation

Typically, a layer of TiN_xO_y of approximately 1 – 2 nm is formed on the film surface[104], which would reduce the effective thickness of the films. X-ray photoelectron spectroscopy was conducted on a 30 nm TiN film grown on MgO to study the oxidation mechanisms on the film surface (Figure 3.5). The N_{1s} , O_{1s} , and Ti_{2p} peaks are decomposed as shown in Figures 3.5b, 3.5c, and 3.5d, respectively. Three peaks can be used to fit the N_{1s} spectrum,

where the dominant peak at 396.8 eV is attributed to Ti-N bonds. The peak at 397.7 eV is due to the formation of an oxynitride compound, resulting in Ti-O-N bonds[105], [117]. An additional weak peak in the fitting is observed at a lower energy 395.8, which may be the result of other impurities or nitrogen chemically bonded on the surface[105], [118]. While evidence of TiN_xO_y is also present in the O_{1s} spectrum (531.2 eV), the main peak at 529.9 eV is indicative of the existence of Ti-O bonds in the films[119]. These results are also corroborated by the decomposition of the Ti_{2p} peak using three pairs of doublets ($2p\ 1/2$ and $2p\ 3/2$) for Ti-N, Ti-N-O, and Ti-O[119], [120] implying that the films are systems consisting of TiN, TiN_xO_y , and TiO_2 . The binding energies and shapes of the peaks in Figure 3.5 are consistent with those reported in literature[105], [117], [119], [120].

To determine how the different oxidation phases possibly modify the optical properties, nine different configurations of an oxide capping layer on a 2 nm thick film are considered. These include oxygen atoms in N substitutional sites (O_N), single oxygen (O_s) and O_2 molecules adsorbed on the surface (Figure 3.6a), and their combination. The corresponding ϵ' plots are collected in panels b) and c). The dielectric function of ideal 2 nm thick layer (i.e. 10L, black thick line) and the corresponding experimental results (black dashed line) are included for comparison.

Since the metallic bands at the Fermi level are mainly due to Ti-derived states, the coordination of Ti atoms is crucial in the resulting optoelectronic properties of the system. If a single or a few O atoms substitute surface nitrogen atoms, this does not substantially change the Ti coordination leaving the electronic structure almost unchanged (Figure 3.6b). O_N is an aliovalent impurity that acts as an n-type dopant, which increases the electron density. Consequently, a blue shift in the crossover wavelength is observed, contrary to experimental results. Conversely, single oxygen atoms on the surface have little effect on the optical properties (Figure 3.6b). On the contrary, O_2 molecules do cause a red shift of the crossover wavelength, tending towards the experimental value (Figure 3.6c). The O_2 molecules change the coordination of the Ti atoms on the surface to resemble the configuration for TiO_2 . As the amount of oxygen is increased, surface Ti easily coordinates with oxygen forming Ti-O bonds at the surface, reducing the overall thickness of pure TiN and leading to the slower blue shift of the crossover wavelengths observed experimentally. To prove this statement we

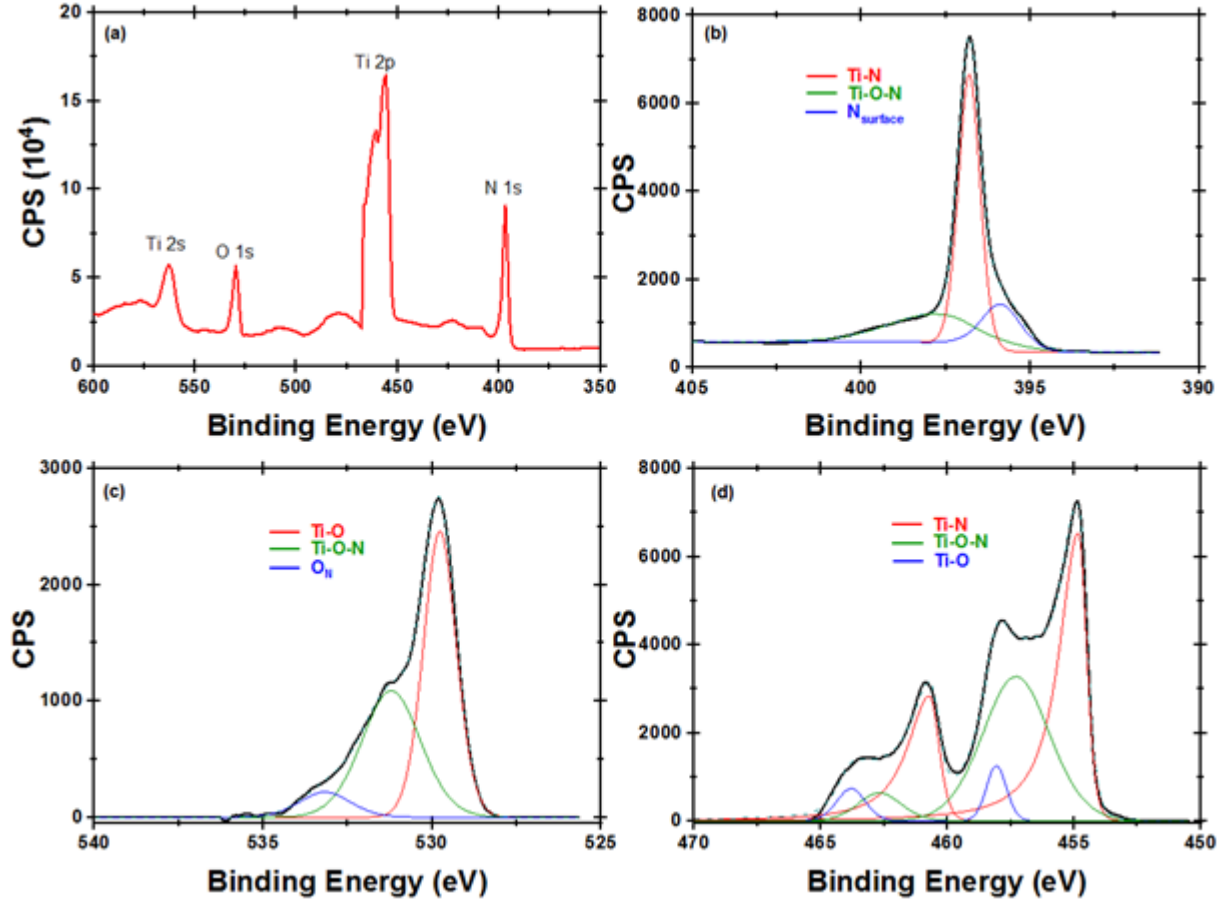


Figure 3.5. (a) XPS spectrum of a partially oxidized 30nm TiN film grown on MgO by DC magnetron sputtering. The (b) N_{1s} , (c) O_{1s} , and (d) Ti_{2p} peaks are fitted to determine the local chemical environment. CPS are the counts per second collected at each energy. The black curve represents the actual XPS data collected, while the blue dashed curve is the generated envelope curve from peak fitting. The films consist of three phases: TiN, TiN_xO_y , and TiO_2 .

consider, as key example, the case where $3O_N$ and $2O_2$ are included in the system (labeled $3O_N+2O_2$, Figure 3.7). After atomic relaxation, the surface layer displays a remarkable structural rearrangement, where the Ti atoms may have three different kinds of coordination: (i) a partially detached oxide layer forms on the surface, where Ti is bonded to O atoms only. This is in agreement with the Ti-O feature revealed in the XPS data (Figure 3.5c). (ii) In the central region of the slab, Ti is 6-fold coordinated with N, and forms the TiN core of the film (see also main peak in Figure 3.5b). (iii) In the intermediate region N and O coexist

and Ti atoms are coordinated with both species giving rise to mixed Ti-N-O phases. This is coherent with the appearance of Ti-N-O features in N_{1s} and O_{1s} spectra.

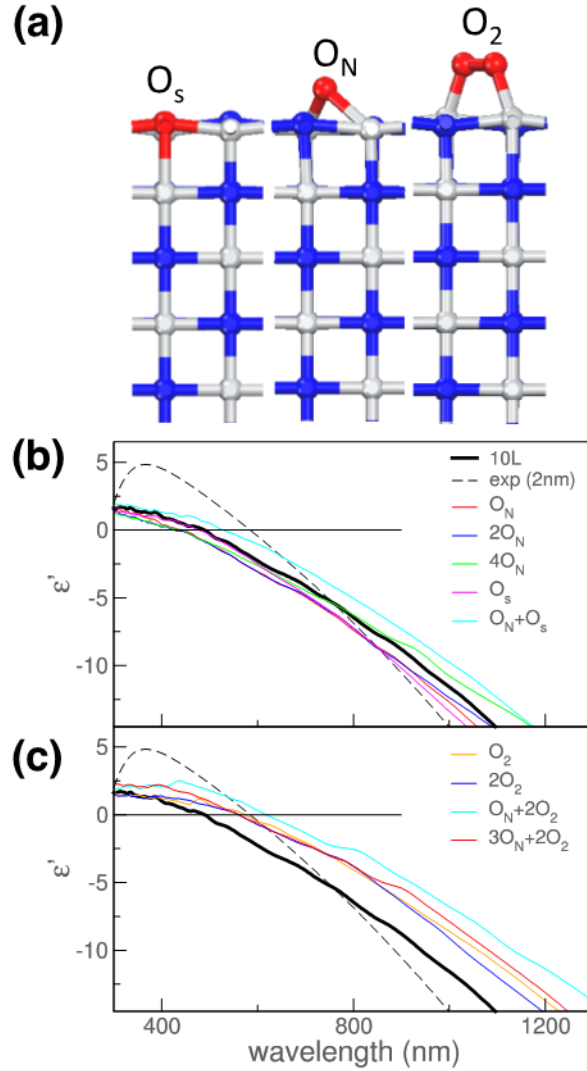


Figure 3.6. (a) Configurations for single oxygen atom in a nitrogen substitutional site (O_N), single oxygen atom on the surface (O_s) or diatomic oxygen molecule on the film surface (O_2). Real part of the dielectric function of oxidized TiN film including (b) single atoms O_N and O_s ; and (c) O_2 molecule. Different combinations of these three main configurations are modeled to determine the effect of oxygen in the films. Theoretical ideal model (10L) and the corresponding experimental spectra are reported in panels b and c for direct comparison.

The effects on the electronic structure are evident in Figure 3.7b, where the comparison with the DOS of ideal 10L system is presented. The total DOS of $3O_N+2O_2$ system is

reminiscent of the original bands **1** - **2** and the system maintains a metallic character, but the presence of oxygen (shaded area) includes new localized states across the Fermi level. This has a twofold effect: first, it reduces the effective thickness of TiN; second, it introduces further O-derived states that contribute to interband transitions, further shifting the crossover wavelength toward red. The oxide layer, however, is not sufficiently thick to exhibit the characteristic dielectric features of TiO₂. Although the exact microscopic reconstruction of the surface strictly depends on the growth process, this example is sufficient to give optical properties in quantitative agreement with experimental findings (Figure 3.6b).

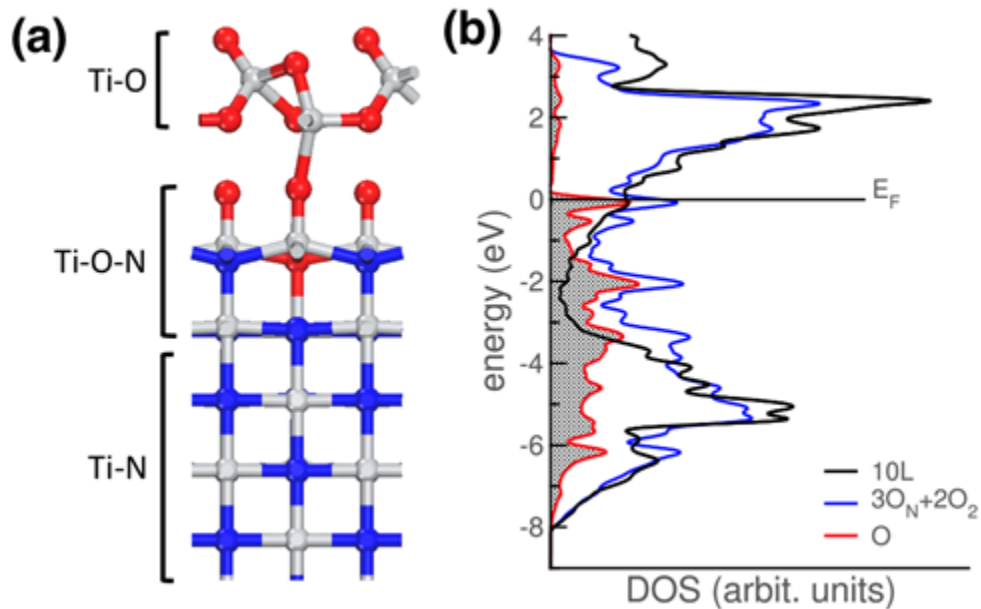


Figure 3.7. (a) Relaxed geometry of 3O_N+2O₂ configuration. (b) Total (blue line) and O-projected (shaded area) density of states of 3O_N+2O₂ configuration compared to the ideal unoxidized 10L case (black line). Zero energy reference is set to the Fermi level of the two systems.

3.3.3 Effect of Substrate Induced Strain

Since experimental TiN samples are not free standing but grown on MgO substrate, the effect of a substrate induced strain is included in the simulations and compared to experiments. The lattice mismatch would introduce a strain in the film, changing the in-plane lattice parameter of TiN. In order to investigate this effect without including other structural

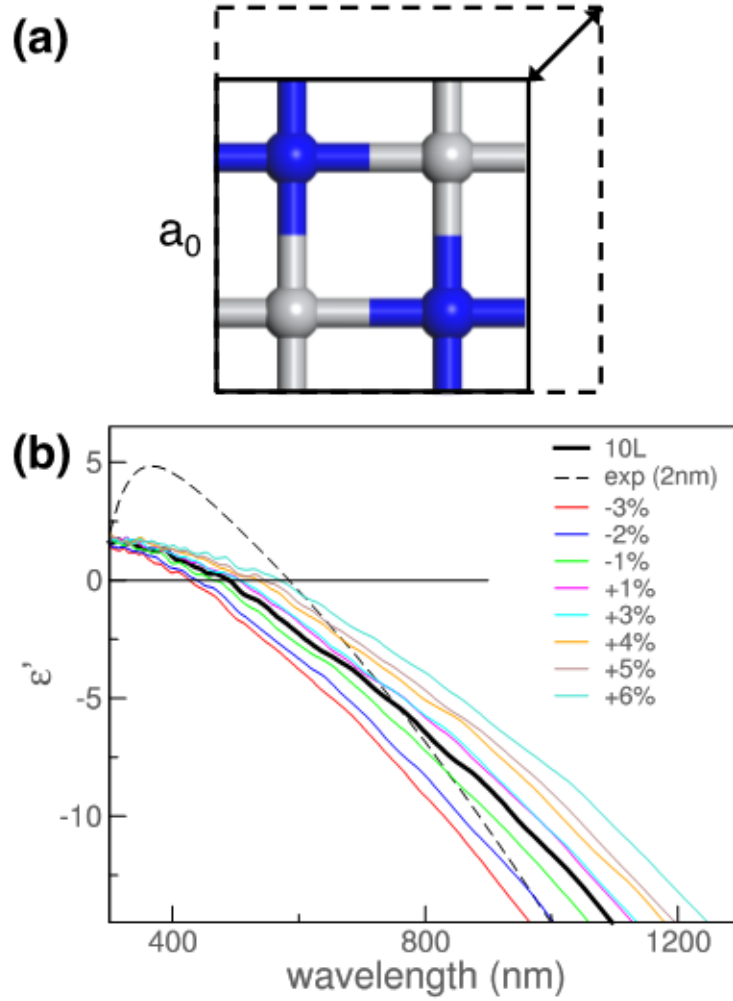


Figure 3.8. (a) In-plane strain model. (b) Simulated real part of the dielectric function for 10L TiN films, with varying amount of applied lateral strain. The crossover wavelength red shifts with tensile strain. Theoretical ideal unstrained model (10L) and corresponding experimental spectra are reported in panels (b) for direct comparison.

modifications derived by the explicit description of the substrate, we simulated a set of free standing 10-layer-thick TiN films with varying in-plane lattice constants, which span the range from -3% to 6%, with respect to the equilibrium lattice parameter ($a_0^{\text{TiN}} = 4.24 \text{ \AA}$), as shown in Figure 3.8. As the lattice parameter is reduced (compressive strain), the crossover wavelength blue shifts; the opposite happens when the lattice parameter is increased (tensile strain). To reach the experimental value for the crossover wavelength, a tensile strain of 6%

is required. Although ultrathin films may sustain large amounts of strain due to interface mismatch, the latter condition (+6%) does not fit the experimental situation as the actual mismatch between TiN and MgO would result in a compressive strain of only 0.7% ($a_0^{MgO} = 4.21 \text{ \AA}$). Thus, even though in principle strain may affect the optical properties of ultrathin films, in the present case oxidation seems to be the most important cause of the differences between the ideal TiN model and measured sample with the same formal thickness.

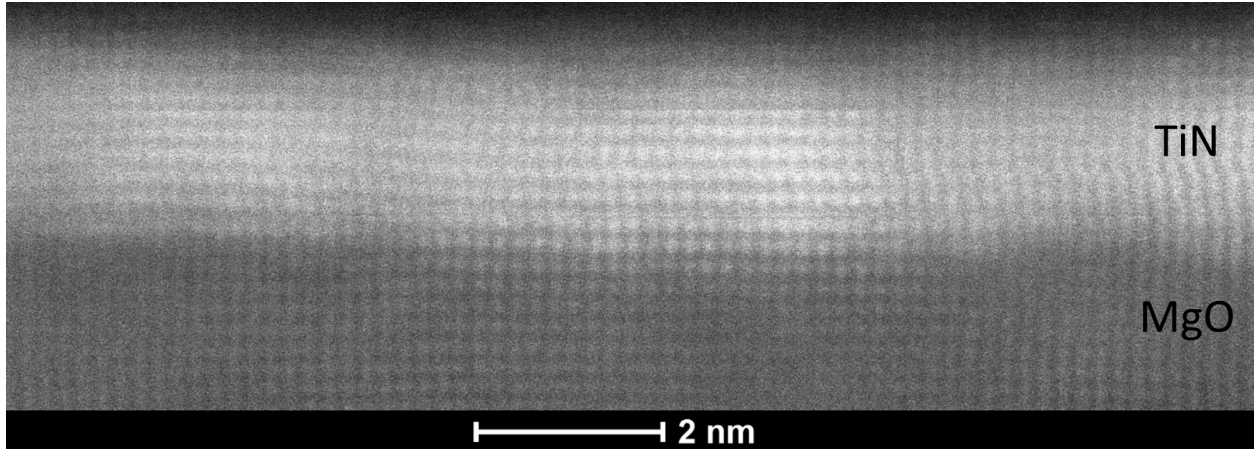


Figure 3.9. HAADF STEM image of a 2 nm TiN film on an MgO substrate. The contrast at the film/substrate interface is due to misfit dislocations, causing the film to relax. This indicated that we do not have any significant contributions from strain in the experimentally characterized optical properties

To support these results, the substrate induced strain is experimentally determined by high-angle annular dark field imaging scanning transmission electron microscopy (HAADF STEM) of a 2 nm TiN film grown on MgO, as shown in Figure 3.9. The observed contrast at the TiN/MgO interface signifies the formation of misfit dislocations, indicating that the film has relaxed and has no substrate induced strain which may have influenced the optical properties. The strain relaxation mechanism is typically dependent on the growth process of the material. If the first few monolayers of TiN grown on MgO formed epitaxial islands having the same crystal orientation, the coalescence of the islands would create dislocations contributing to strain relaxation. Once the islands merge, a smooth, continuous, epitaxial film continues to grow[121], [122]. This is consistent with the theoretical findings that the oxidation plays the main role in the difference between the simulations for pure TiN and

experimental work. However, as the thickness decreases, the films may remain strained and exhibit a stronger effect on the changes in the optical properties.

3.3.4 Effect of the MgO Substrate

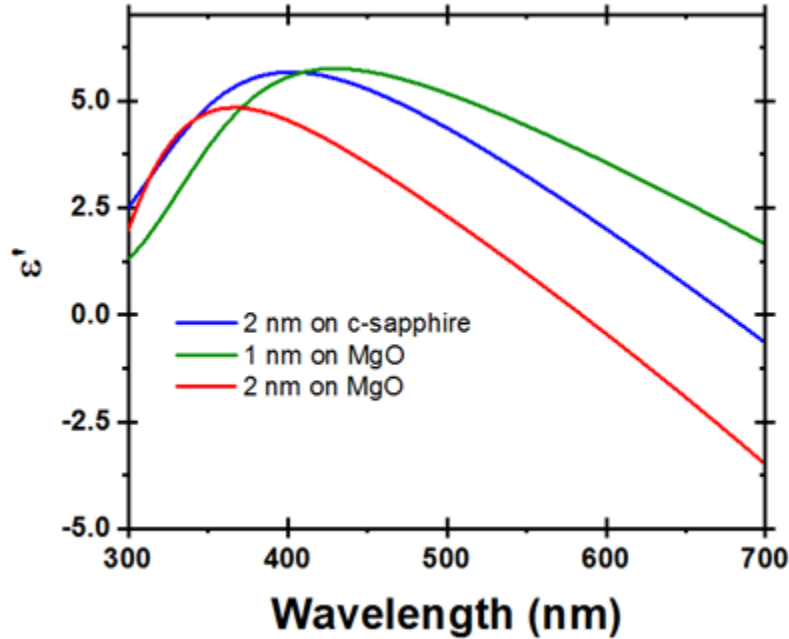


Figure 3.10. Real part of the dielectric function extracted from ellipsometry measurements for ultrathin TiN films grown on MgO and c-sapphire substrate

Although MgO substrate does not affect the position of λ_0 , it acts as a dielectric environment that may change the optical response of TiN films at lower wavelengths ($\lambda < 400$ nm), i.e. where ϵ' is positive and TiN acts as dielectric medium. In the experimental spectra from ellipsometry measurements, we detect a local maximum at 400nm, which is characteristic only of the 2nm and 4nm films. In the thicker films, the local maximum appears at a lower wavelength (320nm). This is consistent with other experimental and theoretical reports for bulk TiN. At smaller thicknesses, the substrate has a more pronounced effect on the permittivity of the films, which is most probably due to a dielectric effect from the substrate. This is expected to be the cause of the enhancement of ϵ experimental values compared to the theoretical ones. The same maximum is also present in films grown on c-sapphire (Figure 3.10), which has a comparable refractive index to MgO. The presence

of the substrate increases the interband transitions in the UV range between substrate and film, which are responsible for the increase of the dielectric function. MgO does not alter the crossover wavelength of the film, which is strictly dependent on the TiN thickness.

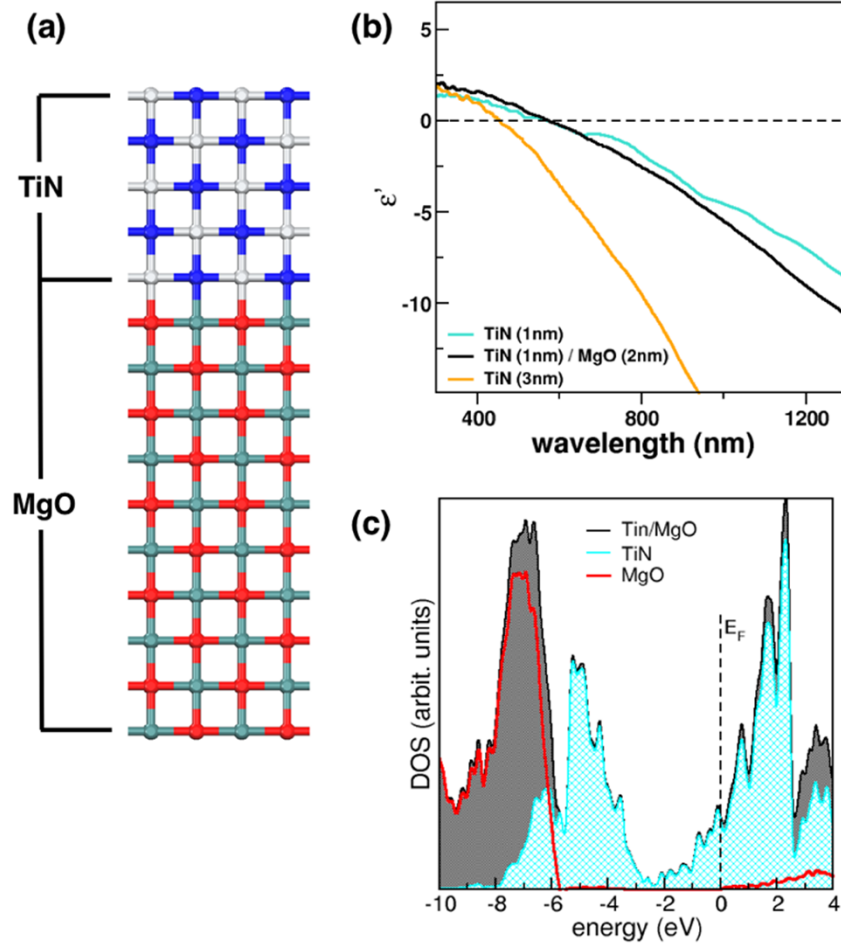


Figure 3.11. Simulated TiN/MgO interface: a) atomic structure (side view); b) real part of the dielectric function; c) total (black area) and TiN- (cyan area) and MgO-projected (red line) density of state. Vertical dashed line marks the Fermi Level (E_F) of the interface.

In order to give a qualitative characterization of the screening effect of MgO substrate on TiN dielectric properties, we calculated the optical properties of a thin TiN/MgO interface. Since TiN and MgO are almost lattice matched, we fixed the lateral periodicity to TiN lattice parameter. The simulation cell, $(4.24 \times 4.24 \times 55.00)^3$, includes 5 layers (1 nm) of TiN(100) and 10 layers (2 nm) of MgO(100), as shown in Figure 3.11a. In order to correct the

well-known bandgap underestimation of standard DFT, we adopted a recent pseudohybrid Hubbard implementation of DFT+U (namely ACBN0 approach [S6]) that profitably corrects the energy bandgap, and the dielectric and vibrational properties of semiconductors [S6]. The U values for Mg and O resulting from ACBN0 cycle and used for the calculations are: $U_{3s}(\text{Mg})=0.52$ eV and $U_{2p}(\text{O})=8.30$ eV, respectively. The resulting band gap for MgO bulk is $E_g=7.46$ eV ($E_g^{\text{exp}}=7.8$ eV) and the dielectric constant $\epsilon^\infty=1.8$ ($\epsilon_{\text{exp}}^\infty=2.9$).

Optical properties of TiN/MgO interface are summarized in Figure 3.11b, which shows the real part of the dielectric function (black line), where we superimposed the results for free standing 1nm-TiN (5L, turquoise line) and 3nm-TiN (15L, orange line), for comparison.

Albeit 2nm-thickness is certainly too small to fully reproduce the overall dielectric properties of the MgO substrate, Figure 3.12 underlines interesting issues: (1) the inclusion of the substrate increases the dielectric response of the system in the UV region of the spectrum, which is due to an enhancement of the joint density of states (not-shown) deriving from TiN $\rightarrow$ MgO interband transitions (see DOS superposition in panel c). (2) MgO does not affect the position of the crossover wavelength, which recovers the same value of free standing 1nm-TiN. (3) The blue shift of crossover frequency as the thickness is increased is mainly associated to the thickness of TiN films and not to the overall interface (i.e. to the substrate). (4) The present model reproduces a perfect interface between perfectly matched surfaces. In this case Ti atoms at the interface maintain their original coordination and do not exhibit the red-shift behavior due to oxynitride compounds.

3.4 Summary

We have conducted a detailed theoretical and experimental study on the plasmonic behavior of ultrathin (down to a few atomic layers) TiN films to determine the role of thickness, surface oxidation and interface strain on TiN optical properties. As the thickness is reduced, the metallic character is also decreased because of quantum confinement effects, which increase the contribution from under-coordinated surface atoms leading to an increased electron localization. The atomistic analysis of the experimentally grown TiN thin films indicates a non-negligible deviation from the ideal TiN structure on the surface. We show that the

fabricated films' composition can be described as a combination of three different phases: titanium nitride, titanium oxynitride, and titanium dioxide. The surface oxidation of the films, particularly affecting the Ti coordination, has a significant influence on the optical properties of the TiN films, which red shifts the crossover wavelength with respect to the ideal case with the same formal thickness. Additionally, although there is no strain observed in the current films studied, thinner films may exhibit a change in the lattice parameter, which would further affect the optical properties. The investigated ultrathin films remain highly metallic and are characterized by plasmonic excitations in the visible wavelength range. More importantly, the fabricated ultrathin films' optical response can be adjusted by controlling their structural and compositional parameters, such as thickness, strain, and oxidation during growth. The observed plasmonic properties, in combination with the confinement effects, make TiN ultrathin films a promising material for the realization of plasmonic metasurfaces with enhanced nonlinearities and electrical tunability.

4. THICKNESS DEPENDENT PLASMONIC PROPERTIES OF PASSIVATED TRANSDIMENSIONAL TITANIUM NITRIDE

4.1 Introduction

To explore the full potential of metallic TDMs for nanophotonic applications, it is critical to gain insights into the role of confinement and dimensionality on light-matter interactions in atomically thin metals. Recently, theoretical studies devoted to elucidating the confinement-related effects in plasmonic TDMs have revealed the thickness dependent optical response and plasmon dispersion of various metals[35]–[37], [40], [41], [123]–[125]. Relevant to our work, a confinement induced nonlocal Drude dielectric response model based on the Keldysh-Rytova (KR) pairwise electron interaction potential was developed to analytically describe the optical properties in ultrathin metal films as they transition from TDMs to 3D materials[40]. Using this nonlocal KR model, remarkable electromagnetic (EM) properties of plasmonic TDMs have been demonstrated, including large dipolar spontaneous emission enhancement[45], resonance magneto-optical response[44], pronounced negative refraction features[44], [126], and low-temperature plasma frequency drop-off[127].

Until recently, experimental progress in studying the thickness-dependent properties of plasmonic TDMs and validating new theories had been limited due to the challenges in growing ultra-smooth, continuous metallic films with thicknesses below 10 nm[60], [64]. The latest developments in material growth techniques have made it possible to achieve continuous atomically thin metals with controlled thickness and low roughness[47], [65]–[67] [64], allowing one to probe the plasmonic properties of TDMs and light-matter coupling as they evolve from a few atomic layers to a bulk material. Among these high quality plasmonic materials, TiN has been established as a promising material platform to investigate the optical properties in the transdimensional (TD) region due to its epitaxial growth[41], [99], [128], [129], refractory properties[72], [130]–[133], and tailorability[105], [134]–[136]. In chapter 2, we reported on the optical and electrical properties of TiN films with thicknesses below 10 nm[61]. However, the surface oxide that naturally occurs on TiN has prevented the separation of the effects from oxidation and thickness on the optical response evolution in TD TiN[41], [104]. An in-situ passivation layer of AlScN, which can be grown epitaxially on

TiN[137], can help to mitigate the issue of oxidation. Here, we present the optical properties of passivated ultrathin TiN films with thicknesses ranging from 1 to 10 nm to explore the thickness dependent trends without any contribution from the oxidation process. We demonstrate the influence of strong confinement on the optical properties of TD TiN and provide the first experimental verification of the thickness dependent plasma frequency induced by electron confinement as predicted by the nonlocal Drude model based on the KR potential.

4.2 Methods

4.2.1 Material Growth

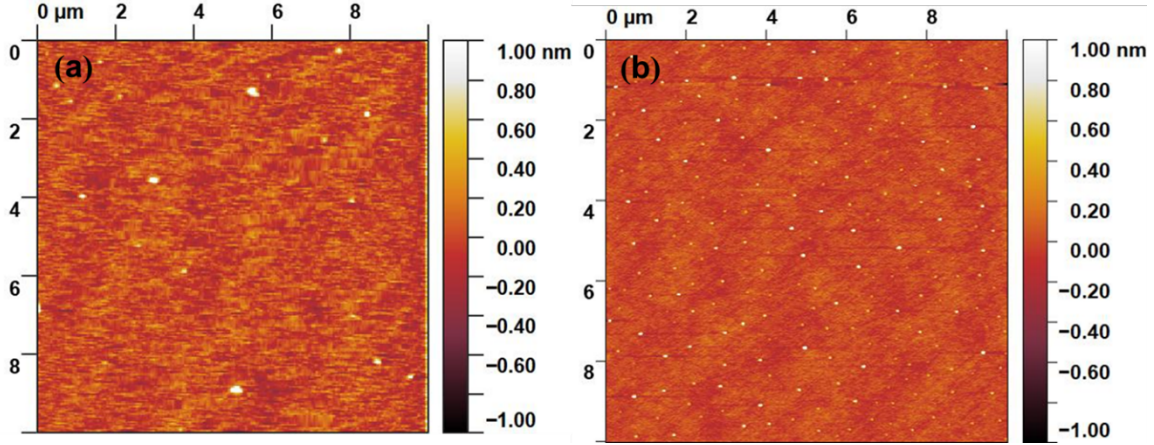


Figure 4.1. AFM images of a 10 nm AlScN film on (a) 2 nm thick TiN film and (b) 8 nm thick TiN film with a root mean square (RMS) roughness of 2.8 Å and 2.7 Å, respectively. The low roughness indicates uniformly passivated and atomically smooth films.

TiN films with thicknesses ranging from 2 to 10 nm were grown on a MgO substrate using DC reactive magnetron sputtering from PVD Products Inc. The TiN deposition was completed by sputter deposition of a titanium target in an 60% nitrogen and 40% argon environment at 5 mT with 200 W of DC power with the substrate heated to 800° C. An in-situ passivation layer of 10 nm AlScN was deposited on the ultrathin films to protect the TiN film from oxidation. AlScN was chosen as the passivation layer since it can be grown epitaxially on TiN[99], [137]. AlScN was grown by co-sputtering Al and Sc targets

in a 60% nitrogen and 40% argon environment at 5 mT at a temperature of 800° C. The Al and Sc targets were ignited at 200W and 130W of DC power, respectively. Atomic force microscopy (AFM) scans of the passivated TiN films reveal atomically smooth surfaces with low roughness below 3 Å (Figure 4.1), indicating a uniform AlScN passivation layer on the TiN films. Epitaxial, ultrathin TiN films deposited on MgO, a lattice matched substrate, as well as epitaxial AlScN, have previously been demonstrated using these same processes[41], [99], [137].

To determine the growth rate, a thick TiN film was deposited on silicon for 100 minutes. The thickness was measured using scanning electron microscopy (SEM), which had a 5% error bar. Subsequently, the sputtering time for the desired thickness was calculated. As shown in the TEM image (Fig. 4.2), this method results in accurate thicknesses for continuous films down to 1 nm. The high crystalline quality is also evident from the TEM image and diffraction pattern in Fig. 4.2.

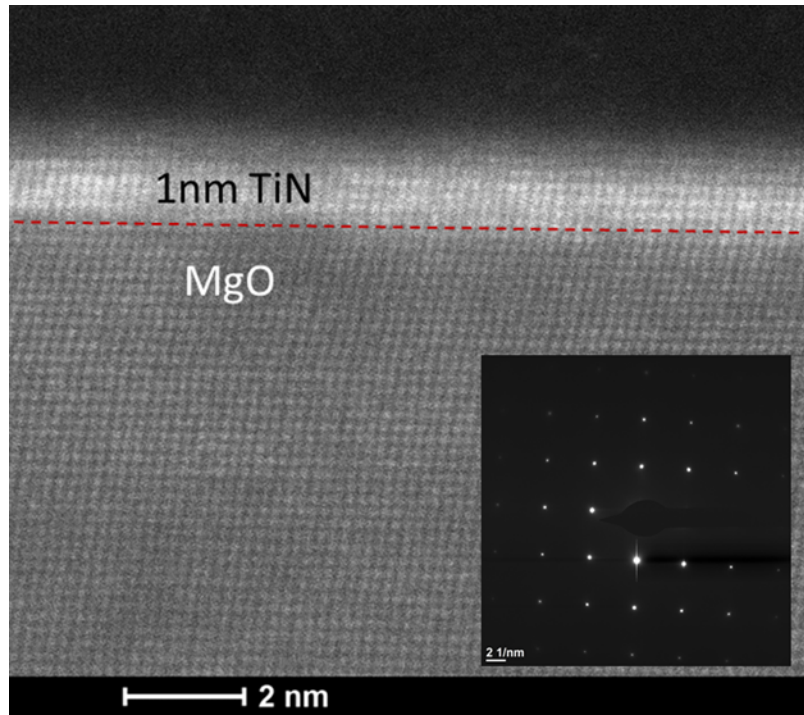


Figure 4.2. High-angle annular dark field imaging scanning transmission electron microscopy (HAADF STEM) image of an epitaxial 1 nm (5 monolayers) TiN film on MgO. The inset shows the diffraction pattern revealing the high degree of crystallinity of ultrathin TiN

4.2.2 Optical Characterization

The optical properties of the AlScN/TiN film stacks were measured at room temperature using a variable angle spectroscopic ellipsometer (VASE) from J. A. Woollam Co. Each measurement was done at incident angles of 50° and 70° for a wavelength range of 400 – 2000 nm. The permittivity of the AlScN passivation layer was first determined by conducting ellipsometry measurements on a 10 nm AlScN film deposited on a 30 nm thick TiN sample with known optical properties. The permittivity of the AlScN layer was fitted using a Lorentz model. The resulting optical constants for the 10 nm thick AlScN film (Figure 4.3) were used for the subsequent fittings of the passivated ultrathin TiN films. The optical properties of the MgO substrate used for the fittings is shown in Figure 4.4.

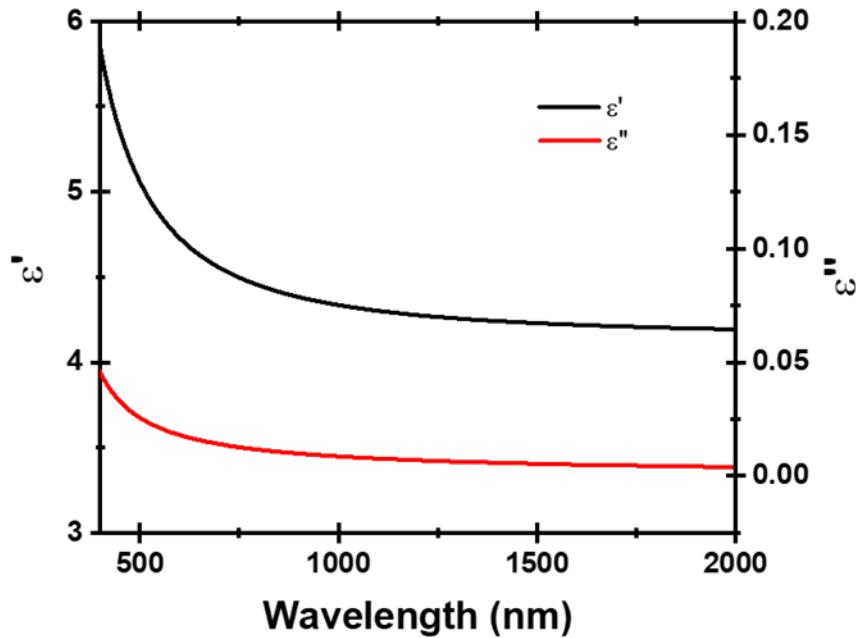


Figure 4.3. Complex permittivity of the AlScN passivation layer used in the ellipsometry fittings for the passivated TiN films

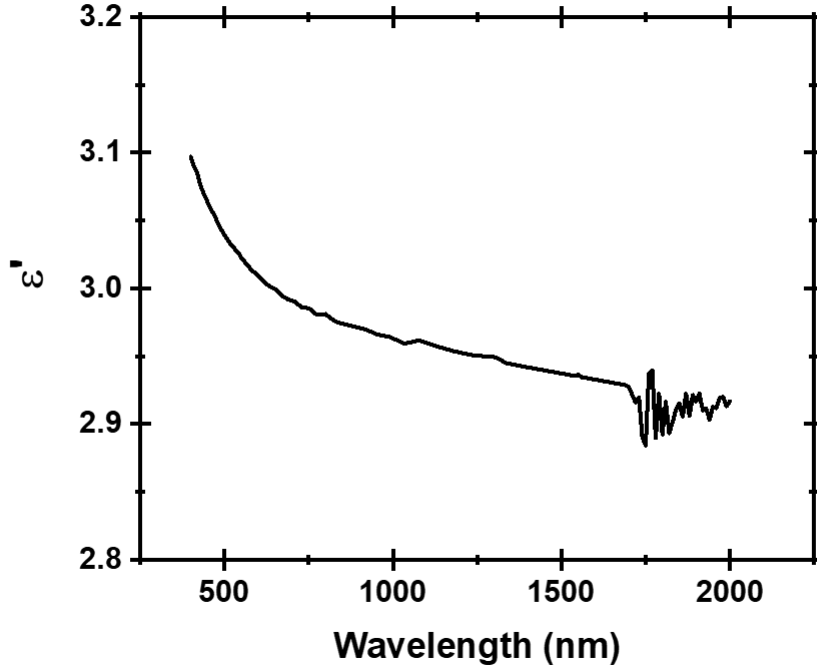


Figure 4.4. Permittivity of the MgO substrate used in the ellipsometry fittings

The optical properties of the TiN films were fitted using a Drude-Lorentz model as discussed in Chapter 2,

$$\varepsilon(\omega) = \varepsilon_b - \frac{\omega_{pD}^2}{\omega^2 + i\Gamma_D\omega} + \sum_L \frac{f_L\omega_L^2}{\omega_L^2 - \omega^2 - i\Gamma_L\omega} \quad (4.1)$$

Since the dielectric functions of the ultrathin TiN films are heavily dependent on the thickness in this regime, the thickness is kept fixed to the deposited target thickness during the ellipsometry fittings. The permittivity of the AlScN passivation layer is also kept fixed as the previously fitted data from the 10nm AlScN/30nm TiN sample.

4.3 Results and Discussion

4.3.1 Thickness Dependent Complex Dielectric Permittivity

The fitted parameters for the Drude – Lorentz model for each of the film thicknesses are provided in Table 4.1. The thickness dependent complex permittivity of the passivated TiN

films measured from ellipsometry is plotted in Figure 4.5(a). With decreasing thickness, the films become less metallic, as signified by the decrease in the absolute value of the negative real part of the permittivity. On the other hand, the imaginary part of the permittivity increases with decreasing thickness in the near infrared range (Fig. 4.5b) because of the increased Drude damping in thinner films.

Table 4.1. Drude - Lorentz fitting parameters for passivated TD TiN films

Thickness (nm)	1	2	4	6	8	10
ε_{inf}	13.8	8.1	8.41	6.17	4.52	5.19
ω_{pD}^2 (eV ²)	47.9	50.65	52.8	54.67	55.71	55.9
Γ_D (eV)	0.40	0.30	0.26	0.237	0.229	0.22
$f_1\omega_1^2$ (eV ²)	14.26	11.6	6.3	56.55	83.38	10.3
Γ_1 (eV)	2.39	0.59	0.45	2.42	1.74	2.8
ω_1 (eV)	0.61	3.7	4.14	4.67	5.02	2.27
$f_2\omega_2^2$ (eV ²)	0.125	23.93	24.27	12.94	20.54	99
Γ_2 (eV)	0.1	5.14	5.06	4.58	6.44	1.55
ω_2 (eV)	3.02	2.65	2.78	1.9	2.9	5.7

As discussed in Chapter 2, the imaginary part of the complex permittivity, ε'' , is dependent on both of the plasma frequency and the Drude damping factor. We experimentally observe a decrease in the plasma frequency and an increase in the damping factor as the thickness decreases as seen from Table 4.1, which will be discussed in more detail in the subsequent sections. Both of these trends would have an opposing effect on the thickness dependent ε'' , since the plasma frequency would result in a decrease in the overall response while the damping factor would cause an increase. At longer wavelengths in the near infrared, we find that the thickness dependent trend of the Drude damping dominates over the plasma frequency the resulting optical behavior as ε'' begins to increase in the thinner films. This is contrary to what we had originally observed for unpassivated films. Due to the oxidation of the films, the carrier concentration and the Drude plasma frequency was decreased much more significantly compared to the changes in the Drude damping factor, resulting in a decrease in ε'' in thinner films. In contrast, for the passivated films, since there is no contribution from oxidation, the decrease in the Drude plasma frequency is solely an effect of strong electron confinement and does not decrease as much. On the other hand,

the thickness dependent Drude damping is quantitatively very similar to what is observed for unpassivated films. Hence, we find that the thickness dependent Drude damping dictates the changes in ε'' .

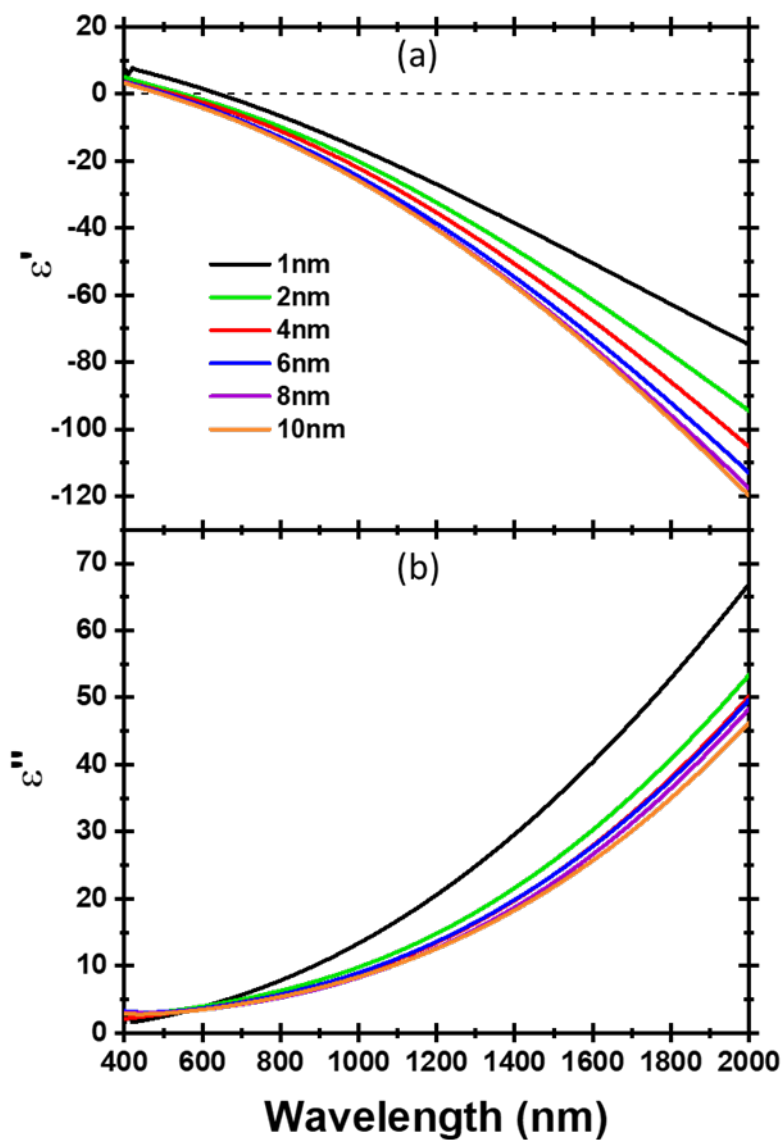


Figure 4.5. Complex dielectric permittivity for different thicknesses measured by ellipsometry. (a) Real part of the permittivity indicates lower metallicity with decreasing thickness. (b) Imaginary part increases with smaller thickness, indicating higher losses in thinner films.

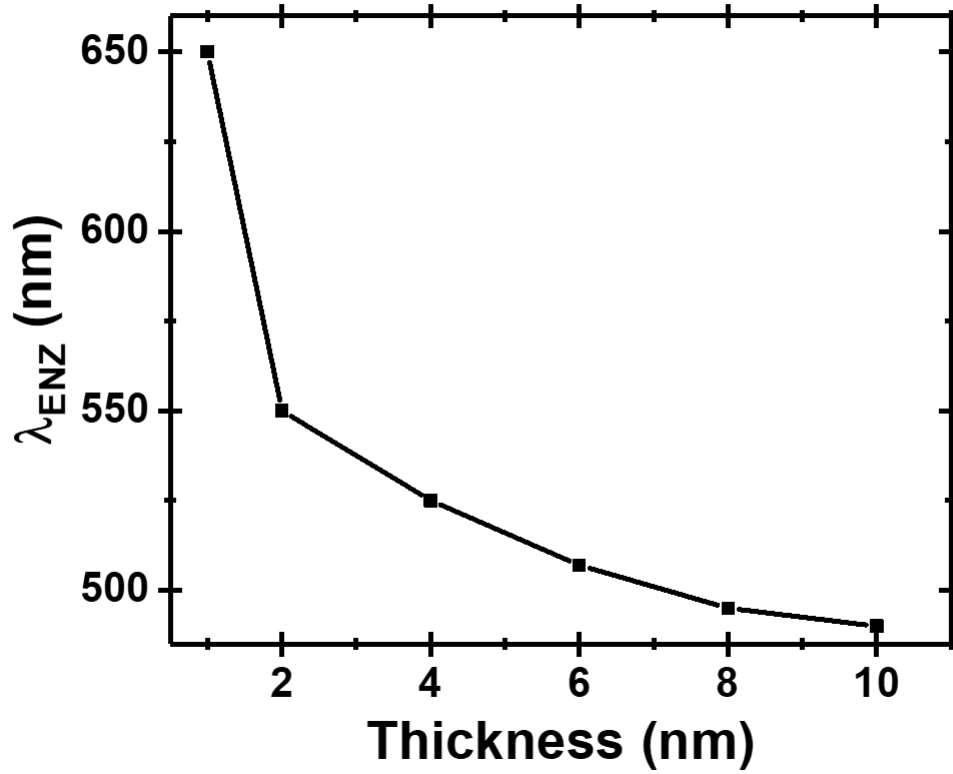


Figure 4.6. Thickness dependent epsilon-near-zero (ENZ) wavelength, which redshifts in thinner films. The experimental trend is consistent with the findings from the DFT studies presented in Chapter 3.

Additionally, as seen in Fig. 4.6, the epsilon-near-zero (ENZ) wavelength where the real part of the dielectric permittivity crosses zero, redshifts in the thinner films from 490 nm for the 10 nm thick TiN film to 650 nm for the 1 nm thick TiN film. The lower metallicity in the thinner films can be attributed to a size dependence caused by the confinement of electrons in the vertical direction. These effects stem from an increase in spatial confinement, which results in a strong Coulomb interaction between confined charges that is described by the KR potential[40], [138]. The role of the KR potential is further expanded on and discussed in terms of the plasma frequency in the next section. First principle density functional calculations (DFT) of unoxidized atomically thin TiN have also revealed a similar redshift of the ENZ in thinner films[41], as discussed in Chapter 3. The redshift in the DFT calculations

is explained by quantum confinement causing modifications to the energy width and position of electronic bands in the density of states.

Similar trends have been demonstrated with earlier experimental and theoretical studies on ultrathin TiN films[41], [61]. In past experiments, the decreasing metallicity in thinner TiN films was explained by a combination of a size effect and a 2 nm thick surface oxide layer on the TiN films. In addition to the spatial confinement modifying the optical response, the presence of the surface oxide on unpassivated films reduced the effective thickness of pure TiN and contributed to the interband transitions, causing a further redshift in the optical properties and ENZ wavelength. In the current study, however, the influence of oxidation is avoided by passivating the films with AlScN allowing us to directly probe the size dependence.

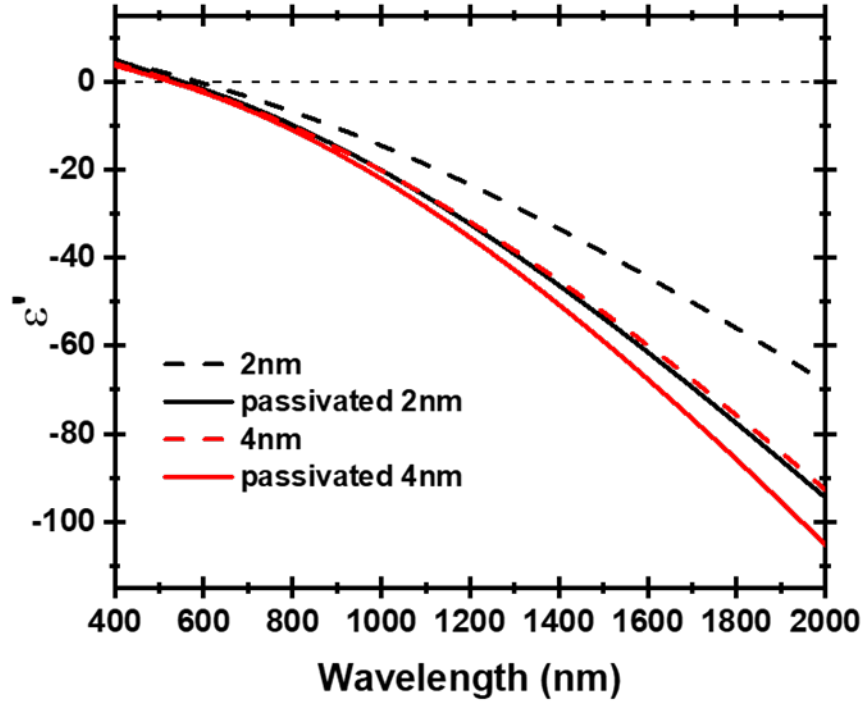


Figure 4.7. Comparison between the real part of the permittivity for unpassivated (dashed) and passivated (solid) films with thicknesses of 2 (black) and 4 nm (red). Passivated films have a larger $|\epsilon'|$, indicating a stronger metallic character compared to unpassivated films because of the absence of oxidation effects.

Due to the absence of the surface oxide, passivated ultrathin TiN films are observed to be considerably more metallic than the TiN films without the AlScN overlayer and show

an increase in the absolute value of the negative real part of the permittivity (Figure 4.7). The ENZ of the unpassivated 2 nm thick TiN film is redshifted by 50 nm compared to the ENZ of the passivated 2 nm thick TiN. The increase in the metallicity of unoxidized films is consistent with predictions from DFT simulations for atomically thin TiN films, where it was demonstrated that the inclusion of an oxide layer in the calculation redshifts the ENZ wavelength[41].

4.3.2 Drude Plasma Frequency

The Drude plasma frequency, ω_{pD} , as extracted from the ellipsometry fitting, redshifts in thinner films going from 7.47 eV for the 10 nm thick film to 6.92 eV for the 1 nm thick film (Fig. 4.8a). To understand the observed dependence of the plasma frequency on the thickness, we use the confinement induced nonlocal Drude dielectric response model recently developed for plasmonic TDMs with finite thickness[40], [44], [45]. Our nonlocal dielectric response model is based on the KR pairwise electron interaction potential[138], [139] to describe charged elementary excitations and their electrostatic interactions in vertically confined TDMs[140]–[143]. The KR potential accounts for the electrostatic interaction between a pair of charge carriers confined in a layer of thickness d , which is mostly due to the dielectric surroundings rather than by the material of the layer itself. When d is less than the typical in-plane distance between the carriers, the electrostatic interaction potential of the charge carriers inside the layer is no longer of the Coulomb form. Instead, it becomes the 2D KR potential with the vertical coordinate dependence (z -coordinate) replaced by the layer thickness d . The dimensionality of the system is then effectively reduced from 3D to 2D. The only remnant of the z direction is the d parameter in the KR potential that represents the vertical confinement size of the system[140].

For the visible to NIR frequencies (below the interband transition frequencies), the Drude-Lorentz in-plane EM response function of an isotropic plasmonic TDMs in Eqn 4.1 can be written as,

$$\frac{\varepsilon(k, \omega)}{\varepsilon_b} = 1 - \frac{\omega_p(k)^2}{\omega(\omega + i\Gamma_D)} \quad (4.2)$$

Here, the Lorentz terms contribute to ε_b , which accounts for the positive ion background screened by inner-shell electrons. The response of the electrons populating the s -band is represented by Eqn 4.2. Additionally,

$$\omega_p(k) = \frac{\omega_p^{3D}}{\sqrt{1 + \varepsilon_1 + \varepsilon_2/\varepsilon_b kd}} \quad (4.3)$$

is the in-plane plasma oscillation frequency of the s -band electron gas with the 2D plasmon momentum $k = |\mathbf{k}|$ in the TDM of thickness d sandwiched between the substrate and superstrate with the dielectric constants ε_1 and ε_2 , respectively. The frequency $\omega_p^{3D} = (4\pi e^2 N_{3D}/\varepsilon_b m^*)^{1/2}$ represents the plasma oscillations in bulk (3D) plasmonic material, where N_{3D} and m^* are the volumetric electron density and electron effective mass, respectively. Equation 4.3 is spatially dispersive, or nonlocal, to result in the nonlocal EM response in Eqn. 4.2. It covers both ultrathin ($d \rightarrow 0$) and thick ($d \rightarrow \infty$) film regimes, yielding the $\sqrt{k}$ and k -independent plasma frequency dispersion for the former and the latter, respectively. This contrasts sharply with standard local Drude-type models commonly used to analyze experimental data[33], [96], including the Drude-Lorentz Eqn. 4.1 utilized here for the studied TiN films. The nonlocality of Eqn. 4.3, which is linear in small k , comes from the strong vertical confinement[44], [144]. This first order nonlocality is much stronger than the second order nonlocality originating from the k^2 dependence of the electron pressure term in hydrodynamical Drude models[145], [146].

At finite temperature, plasmons populate the k -states of the reciprocal space according to the Bose-Einstein distribution function. Therefore, to align the k -dependent theoretical model in Eqn 4.2 with the experimental plasma frequency that assumes no k -dependence in Eqn. 4.1, thermal averaging must be performed on Eqn. 4.2. Under continuous low-intensity light illumination, the plasmonic film is in thermal equilibrium. The standard thermal averaging procedure of Eqn. 4.2 reduces to the plasma frequency averaging over k in Eqn. 4.3 that gives:

$$\bar{\omega}_p(d, T) = \frac{\int_0^{k_c} dk k \omega_p(k) n(k)}{\int_0^{k_c} dk k n(k)}, n(k) = \frac{1}{e^{\hbar \omega_p^{3D}/k_B T} - 1} \quad (4.4)$$

where the numerator sums up all boson plasma frequency modes with different k and the denominator provides the total number of such modes in the 2D reciprocal k -space. The k -space is bounded above by k_c , the plasmon cutoff parameter. The Bose distribution function $n(k)$ controls the plasmon occupation numbers of the k -states in the reciprocal space at fixed finite T .

Plugging in Eqn. 4.3 in Eqn. 4.4 gives the expression

$$\bar{\omega}_p(d, T) = \omega_p^{3D} \frac{\int_0^1 dt \frac{t^{3/2}}{\sqrt{t+1/a}(e^{\lambda\sqrt{t/(t+1/a)}} - 1)}}{\int_0^1 dt \frac{t}{e^{\lambda\sqrt{t/(t+1/a)}} - 1}}, \quad (4.5)$$

where the dimensionless quantities $t = k/k_c$, $\lambda = \hbar\omega_p^{3D}/k_B T$ and $a = \varepsilon_b k_c d / (\varepsilon_1 + \varepsilon_2)$ are introduced for simplicity. This expression was recently used to explain a peculiar plasma frequency T -dependence observed for 100 nm thick TiN films at cryogenic temperatures[129]. In the case of the ultrathin films here, the quantity a is expected to be less than unity. Additionally, the largest contribution to the integrals comes from the region $t \ll 1$. Then, $at \ll 1$ and $\lambda\sqrt{t/(t+1/a)} \approx \lambda\sqrt{at} < 1$ unless λ is sufficiently large to invert the sign of this inequality (which is the case of cryogenic $T < 10$ K reported earlier[127]). In our experiments that are conducted at room- T , this inequality is very likely to be fulfilled as written. Thus, the Taylor series expansion of the exponentials yields

$$\bar{\omega}_p(d) = \frac{\omega_p^{3D}}{2 \int_0^1 dt \sqrt{t(t+1/a)}} \quad (4.6)$$

to the first nonvanishing order in small $\lambda\sqrt{t/(t+1/a)}$, whereby the T -dependence cancels out and the d -dependence stays. For ultrathin films at room- T , Eqn. 4.4 loses its T -dependence and takes the form

$$\bar{\omega}_p(d) = \frac{2C^2 d^2 \omega_p^{3D}}{(1 + 2Cd) \sqrt{Cd(1 + Cd)} - \sinh^{-1}(\sqrt{Cd})} \quad (4.7)$$

with $C = \varepsilon_b k_c / (\varepsilon_1 + \varepsilon_2)$, to give the $\sqrt{d}$ behavior in the ultrathin regime.

The ellipsometry data can now be understood in terms of Eqn. 4.5. We note that the standard data fitting expression in Eqn. 4.1 used to extract the data points shown in Fig. 4.4a assumes a slightly different definition for the bulk plasma frequency parameter ω_{pD} than ω_p^{3D} in Eqn. 4.3. Therefore, we normalize the ω_{pD} data points in Figure 4.4a by 7.6 eV, which is the bulk plasma frequency of TiN as extrapolated from Fig. 4.4b. The black dashed line in Fig. 4.4b shows the ratio as given by Eqn. 4.5 with C taken to be 7.7 nm^{-1} . We find that the theoretical and experimental d -dependences presented in Fig. 4.4b agree quite well. With the fitted C parameter, ε_b can be evaluated. As the surrounding dielectrics are both weakly dispersive, their static permittivities are approximated as those at a wavelength of 650 nm, where the plasmon resonance condition $\text{Re}(\varepsilon) = 0$ is realized in the thinnest film. At 650 nm, $\varepsilon_1 = 3.0$ for the MgO substrate and $\varepsilon_2 = 4.6$ for the AlScN superstrate. We use $k_c = 6.4 \text{ nm}^{-1}$ for the plasmon cutoff as reported recently from the comparison of the Drude model with the first-principles calculations of the low-energy plasmon mode in bulk TiN[90]. We obtain $\varepsilon_b = 9.1$ for the background static permittivity of bulk TiN, yielding $\omega_p^{3D}(\text{TiN}) = 7.6/\sqrt{9.1} = 2.5 \text{ eV}$, which is in very good agreement with both first-principles calculations (2.5 eV, Ref.[89]) and with the electron-energy-loss spectroscopy measurements (2.8 eV, Refs.[82], [83]). For comparison, $\varepsilon_b = 9.5$ and 4 were earlier reported for gold[33] and silver[43], respectively, within the standard local Drude model with no confinement induced nonlocality.

The experimentally measured thickness-dependent plasma frequency agrees well with the predictions of the nonlocal Drude model built on the KR pairwise electron interaction potential. The model stems from a confinement induced effect that results in the $\sqrt{d}$ dependence of the plasma frequency. This is a unique microscopic property of plasmonic TDMs that cannot be obtained macroscopically by imposing boundary conditions on the bulk film interfaces. Similar thickness-dependent plasmonic properties have recently been observed experimentally for ultrathin films of silver[47] and gold[58]. They were interpreted in terms of the standard local Drude model that was adapted to incorporate the known 2D plasmon dispersion[47] and yield the $\sqrt{d}$ dependence for the plasma frequency. While this model can be justified for ultrathin plasmonic films only, the proposed nonlocal Drude dielectric

response model can be applied to all thicknesses covering both the TDM regime as well as conventional thin and thick films.

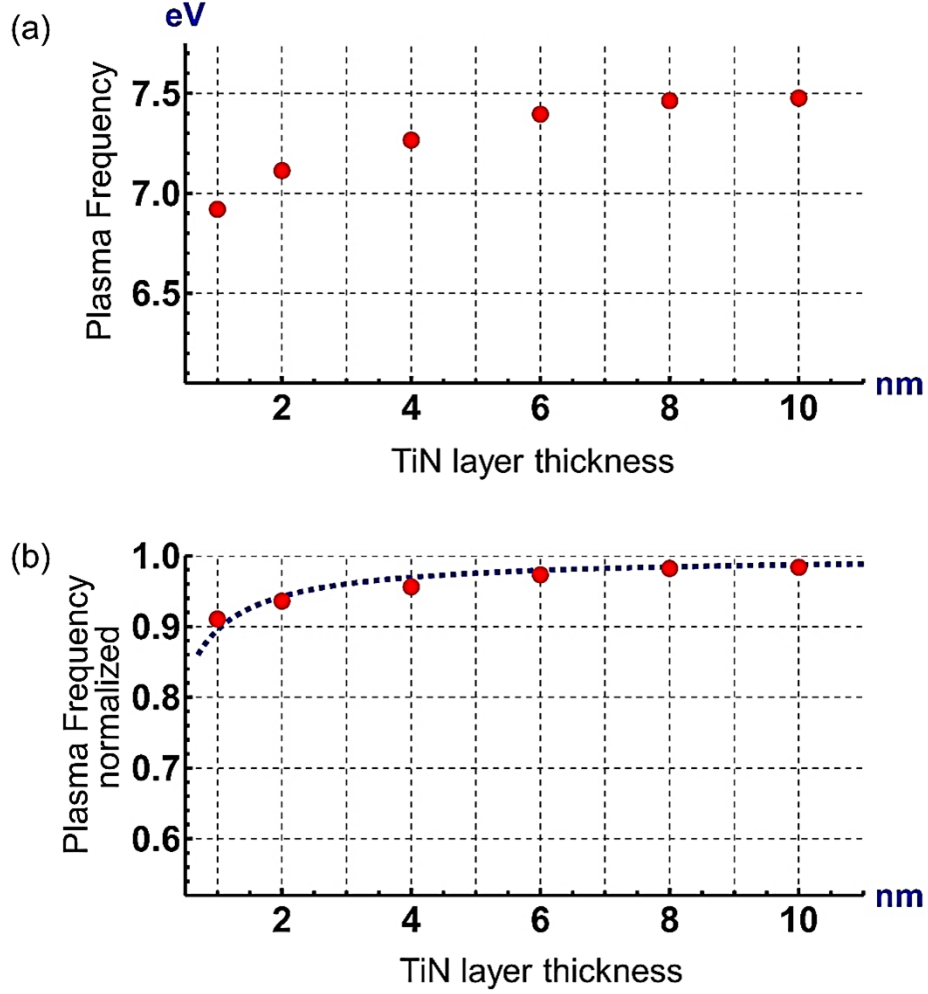


Figure 4.8. (a) The plasma frequency data points extracted from the ellipsometry spectra measured for ultrathin TiN films of different thicknesses. (b) The data point set of (a) normalized. The black dashed line shows the ratio $\bar{\omega}_p(d)/\omega_p^{3D}$ as given by Eqn. 4.5 with parameter $C = 7.7 \text{ nm}^{-1}$. The theory agrees very well to the experiments, indicating that our experiments demonstrate confinement induced optical properties in TD TiN

4.3.3 Thickness Effect on Drude Damping

We retrieve the Drude damping factor, which is the relaxation rate of the free electrons, from the ellipsometry measurements and subsequent fitting. For thinner films, an increase

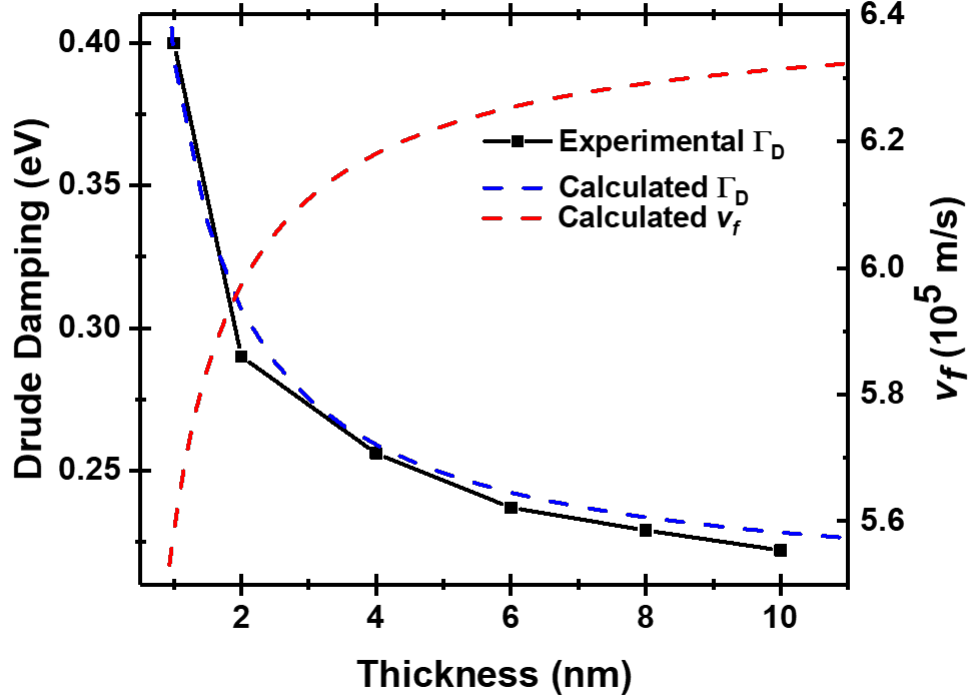


Figure 4.9. Thickness dependent Drude damping factor from ellipsometry measurements (black squares), from calculations (blue dashes), and calculated Fermi velocity, v_f (red dashes). The increase in Drude damping in thinner films is a result of an increase in surface scattering and larger contribution from surface roughness effects.

in the Drude damping factor is observed (Fig. 4.9). The change in the losses of the thinner films is attributed to a decreased effective mean free path caused by an increase in scattering events. The Drude damping is described by the energy dissipation due to free electron scattering via different mechanisms and can be represented by the sum of the contributing processes,

$$\Gamma_D = \Gamma_{e-e} + \Gamma_{e-ph} + \Gamma_{surf} + \Gamma_{def} + \Gamma_g \quad (4.8)$$

where Γ_{e-e} is the electron-electron scattering, Γ_{e-ph} is the electron-phonon scattering, Γ_{surf} is the surface scattering, Γ_g describes the scattering at grain boundaries, and Γ_{def} is the defect scattering. Since the ultrathin TiN films are single crystalline and passivated, the

losses due to grain boundaries and defects are negligible. In bulk epitaxial TiN, the losses, Γ_{bulk} , are dominated by the first two processes (Γ_{e-e} and Γ_{e-ph}). In films with thicknesses smaller than the bulk mean free path l_{bulk} , which is approximately 45 nm for TiN[92], [147], surface scattering increases, resulting in a smaller mean free path[148],

$$l_{eff} = d(\ln(\frac{l_{bulk}}{d}) + 1) \quad (4.9)$$

Considering the thickness dependent mean free path, the losses due to surface scattering in TDMS can be defined as[74]

$$\Gamma_{surf} = \frac{\hbar v_f}{l_{eff}} \quad (4.10)$$

where the Fermi velocity, v_f , can be evaluated from the free electron gas model,

$$v_f = \frac{\omega_p}{k_c} \quad (4.11)$$

Although the films studied are atomically smooth and have a very low roughness of 2-3 Å, the surface roughness may have a significant contribution to the Drude damping for thicknesses as small as 1 nm. Since the roughness stays the same with decreasing thickness, the effect of the surface roughness is expected to be inversely proportional to the film. Then, the overall Drude damping factor for an ultrathin film can be described as

$$\Gamma_D = \Gamma_{bulk} + \frac{\hbar v_f}{l_{eff}} + \frac{A}{d} \quad (4.12)$$

where A is a fitting constant to account for the surface roughness, Γ_{bulk} is assumed to be 0.2 eV from the ellipsometry fitting of an optically thick film of 100 nm TiN. Eqn. 4.10 is fitted to the experimentally retrieved Drude damping, resulting in $A = 0.12$ nm eV. Using Eqn. 4.9, 4.11, 4.12 and the thickness dependent plasma frequency, the Fermi velocity and theoretical Drude damping are plotted as a function of thickness in Fig. 4.9. The calculated Drude damping follows the experimental trend reasonably well, indicating that the ellipsometry results can be well explained by the effect of surface scattering in thinner films. Slight disagreement can be ascribed to the constant $k_c = 6.4$ nm⁻¹ (bulk TiN value)

we used throughout the entire range of thicknesses. For thinner films, k_c is expected to decrease due to the Fermi surface shrinkage caused by the size reduction. As the thickness approaches the TD regime below the mean free path, surface scattering events increase and begin to play a dominant role in the losses of the ultrathin plasmonic films.

4.3.4 Drude Damping in Unpassivated Films

Unpassivated TiN films grown using DC magnetron sputtering on MgO substrates are atomically smooth with a roughness of around $2.1 \text{ \AA}$, as shown in the AFM image in Fig. 4.10. This surface roughness is on par with that of the passivated films with an AlScN overlayer. Hence, the contribution of the surface roughness to the Drude damping in passivated and unpassivated should be similar. The Drude damping of unpassivated films as extracted from ellipsometry is plotted in Fig. 4.11. The thickness dependent Drude damping in unpassivated films does not vary significantly from the Drude damping of passivated films. It follows the same trend of increasing Drude damping with thickness, indicating that surface scattering should be the dominant process that contributes to the losses in ultrathin TiN.

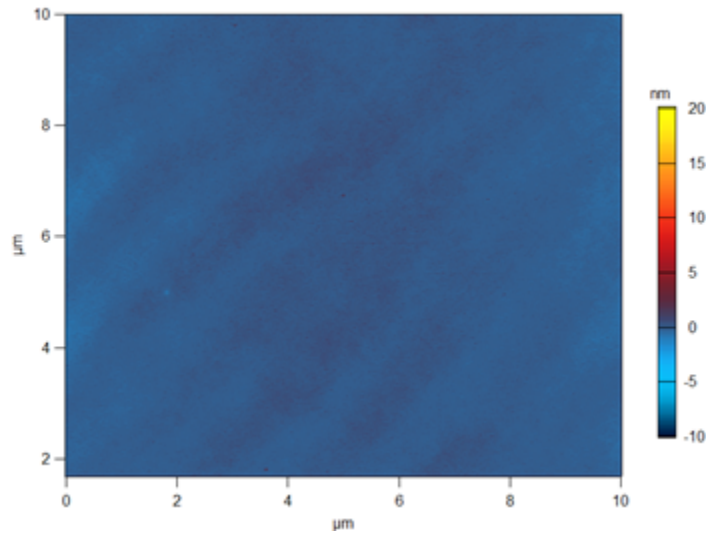


Figure 4.10. AFM image of an unpassivated 4 nm TiN film showing atomically smooth surface with a roughness of $2.1 \text{ \AA}$. The surface roughness of unpassivated films is very similar to passivated films, indicating that the contribution of surface scattering to the Drude damping should be similar.

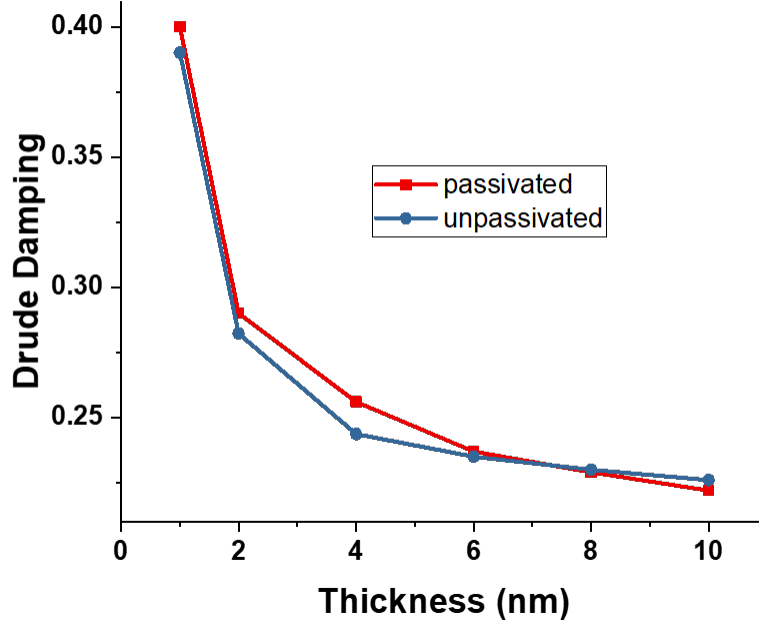


Figure 4.11. Comparison between the thickness dependent Drude damping of passivated (red) and unpassivated (blue) ultrathin TiN films, as extracted from the ellipsometry fittings. Due to similar surface roughness in both types of films, the trends in Drude damping are quantitatively very similar for passivated and unpassivated films.

4.4 Summary

We report on the thickness-dependent optical properties of passivated transdimensional plasmonic TiN with thicknesses down to 1 nm, or 5 atomic layers. The in-situ passivation layer of AlScN helped to decouple the effects of oxidation and electron confinement in the studied TiN films. The ultrathin films become less metallic as the thickness decreases to 1 nm with a redshift in the epsilon-near-zero wavelength because of quantum confinement, which is consistent with previous theoretical studies^{20,21}. We observe an increase in the Drude damping coefficient due to surface scattering and a decrease in the Drude plasma frequency. The passivated 1 nm thick TiN films remain plasmonic in the visible and NIR range with a ENZ wavelength at 650 nm. More importantly, the thickness-dependent plasma frequency retrieved from the ellipsometry measurements matches very well with the confinement in-

duced nonlocal Drude model. In this model, the vertical electron confinement changes the electron-electron Coulomb potential into the much stronger KR potential and results in the $\sqrt{d}$ plasma frequency dependence in the ultrathin film regime. Our experimental demonstration of thickness dependent optical properties in TD plasmonic TiN provides a crucial step in realizing high quality atomically-thin metallic films that exhibit new material functionalities and unique light-matter interactions. The quantum effects that arise in metallic TDMs along with their strong tunability may pave the way to new optical phenomena and novel, atomically-thin, dynamically tunable nanophotonic devices. Specifically, plasmonic TDMs hold immense potential for enabling a new generation of tunable metasurfaces that utilize strong confinement and nonlocal effects.

5. TRANSDIMENSIONAL TITANIUM NITRIDE FOR ACTIVE METASURFACES

Part of the content presented in this chapter is taken verbatim from the paper H. Jiang, H. Reddy, D. Shah, Z. A. Kudyshev, S. Choudhury, D. Wang, Y. Jiang, A. V. Kildishev, “Modulating phase by metasurfaces with gated ultra-thin TiN films”, *Nanoscale* 11 (23), 2019.

5.1 Introduction

Dynamic modulation of the optical response in metals has been a long-standing challenge in plasmonics. In the absence of interband transitions, the optical properties of metals are primarily determined by the free electrons. Typically, the free electron densities in metallic materials (with negative real part of epsilon) are large, of the order of 10^{22} cm^{-3} which is the major hurdle for dynamic modulation of the optical properties. However, as recently predicted[33], the free carrier densities, and thereby the optical response itself, can be significantly tuned with conventional gating techniques, provided that the metal film is only a few monolayers in thickness. To push the realm of electrical control from the far-/mid-IR to the telecommunication and visible wavelengths, plasmonic TDMs, which are more metallic than graphene are required. The key challenge has been to produce continuous films that are only a few monolayers in thickness and retain their plasmonic behavior in the visible and NIR range. Recently, the dynamic modulation of plasmonic resonances in atomically thin metals has been experimentally demonstrated in 3 nm thick gold nanoribbons[58]. Additionally, as demonstrated in the previous chapters, epitaxial, atomically flat ultra-thin TiN films with thickness down to 1 nm can be routinely grown. Here, we demonstrate that active tuning of the charge carrier concentration in a 1 nm TiN film can be achieved by performing gate dependent Hall measurements. Based on the modulation of the carrier concentration that can be achieved, a phase modulator based that can achieve 337° phase modulation at $1.55 \mu\text{m}$ on a 1 nm TiN film is designed.

5.2 Electrical Tunability of Atomically Thin TiN

We have performed preliminary calculations to predict the possible electrical tuning of the charge carrier concentration in TD TiN. Using the bulk carrier density, the areal density in ultra-thin films was computed. A doping density of 10^{14} cm^{-2} is assumed, which can be routinely achieved with the existing gating technologies. The ratio of this doping density to the areal density gives the relative change as shown in Figure 5.1. Our initial calculations based on the voltage dependent studies indicate that close to 15% tunability can be achieved in a monolayer of TiN with currently available gating techniques. It should be noted that the bulk carrier density was used in these calculations. However, in such thin films the carrier density is expected to be lower than bulk, as discussed in Chapters 2 and 3. As a result, we may see an even larger relative change in the density.

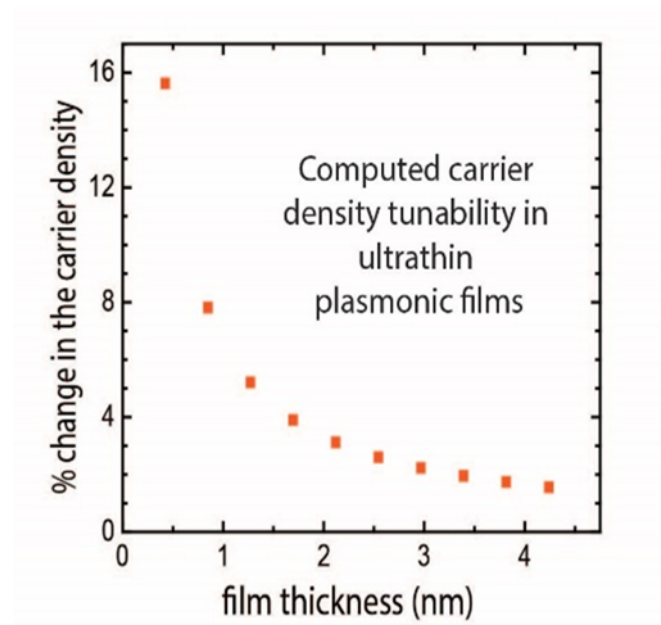


Figure 5.1. Calculations of relative changes in carrier densities achievable in TiN through electrical gating for varying film thicknesses. Close to 15 % relative change is expected in case of monolayer TiN

Gate dependent Hall measurements on a 1 nm TiN film were performed to test the feasibility of electrical control. The fabricated device consisted of four gold arms connected to the ends of the Hall cross, which served as the electrodes. A 35 nm thick alumina layer

grown using atomic layer deposition (ALD) was used as the top gate oxide. A fifth gold arm is used for the top gate electrode. The schematic of the gate dependent Hall measurements is shown in Figure 5.2b. We observe close to 8.5% change in the carrier density in 1 nm TiN films, as plotted in Figure 5.2a.

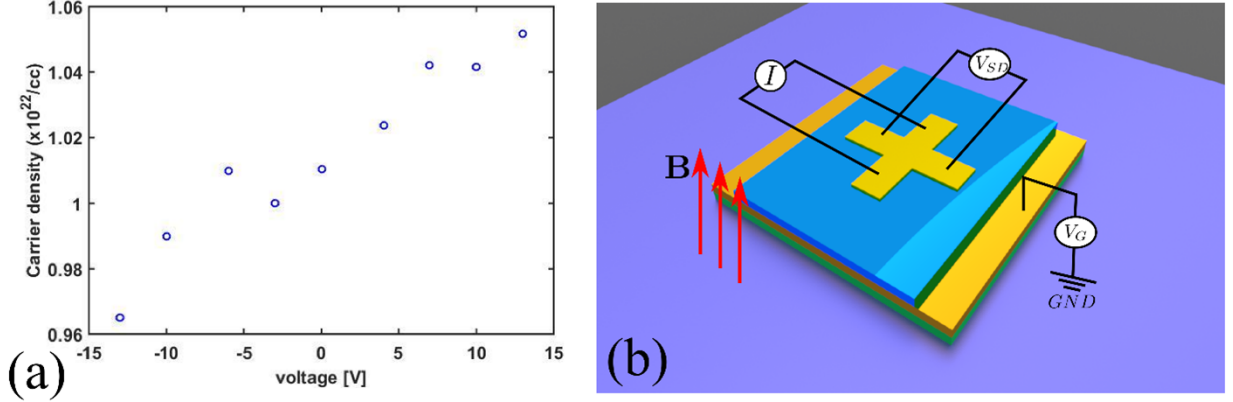


Figure 5.2. (a) Experimentally retrieved carrier density as a function of bias gate voltage in 1-nm-thick TiN film with close to 8.5% change in carrier density; (b) schematic of the gate dependent Hall measurements. A 35-nm-thick layer of Al_2O_3 is used as the gate oxide and gold as the back-gate electrode.

5.3 Phase Modulation with Atomically Thin TiN

A dynamically tunable phase modulator was designed based on the tunability of atomically thin TiN. The phase modulation metasurface consists of an array of Au strips with a width of 258 nm and a 50 nm thickness placed on top of a 1 nm thick TiN film separated by a 45 nm Al_2O_3 spacer from a Au underlayer, which supports gap plasmon modes as schematically shown in Fig. 5.3a. To design our dynamic phase modulator, the carrier density in 1 nm thick TiN films was reduced by 12%, a number that is achievable with existing gating approaches. The calculated reflection coefficients and phases of the optimized structure with the TiN carrier densities reduced by 6% and 12% along with the unperturbed TiN film (0% change in carrier densities) are shown in Fig. 5.3b. As the TiN carrier density decreases, the reflection dip displays a slight blueshift as shown in Fig. 5.3b. The near zero reflection coefficient and 180° phase shift near or at $1.540 \mu\text{m}$ marked by 6% in Figs. 5.3b represent

the critical coupling state of the optimized structure. The reflection coefficients with the unperturbed and 12% lower carrier density are both larger than the 6% case at resonant wavelength, which demonstrates the breaking of balance between the resonant scattering channel and non-resonant channel. By increasing the TiN carrier density, the critical coupling state of the Au strip-TiN film hybrid metasurface moves into an over-coupling state, and the phase evolves from 180° to 0° , and ultimately to -180° at $1.552 \mu\text{m}$. With increasing TiN carrier density (red curve), the metasurface covering a 140° phase shift at $1.526 \mu\text{m}$ moves into the under-coupling state. Therefore, along with the realization of different coupling states by gating ultrathin TiN films, the reflection phases are dynamically modulated at certain wavelengths.

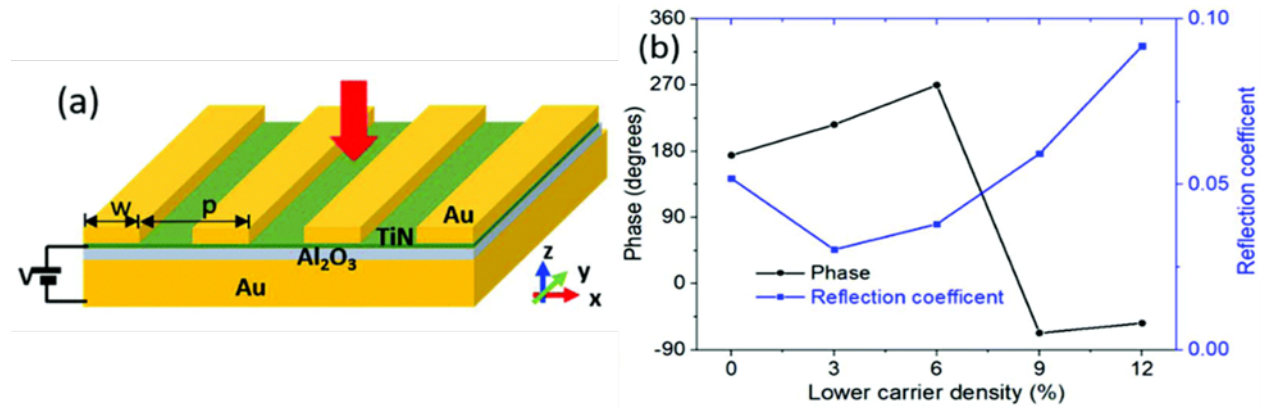


Figure 5.3. (a) Schematic of Au strip-TiN film hybrid metasurface. (b) Change in reflection phase and coefficient at $1.550 \mu\text{m}$ as a function of the change in charge carrier density. A phase modulation of $>300^\circ$ is achieved by lower the charge carrier density from 6% lower to 9%

5.4 Summary

The electrical tunability of the charge carrier concentration in atomically thin TiN has been demonstrated. Based on the theoretically achievable changes in the charge carrier density, the designed dynamic metasurface design enables $>300^\circ$ phase modulation at $1.55 \mu\text{m}$, which is achieved by using realistic numbers for carrier density changes in 1 nm thick TiN film. Despite the significant progress made in optical and electrical modulation, the development of active metasurfaces in the visible and near-infrared wavelength ranges is

still greatly pursued, as these are spectral regions of utmost importance for sensing and optical signal processing technologies. Ultra-thin TiN film, an emerging electrically tunable material, offers an alternative material platform to realize dynamic light manipulation in the visible and NIR wavelength ranges.

6. Conclusion and Outlook

This thesis describes the development and characterization of plasmonic atomically thin TiN for tunable nanophotonic devices. We have experimentally demonstrated transdimensional TiN films down to thicknesses of 1 nm that retain their plasmonic behavior in the visible and near-infrared wavelength range. Moreover, the thickness dependent optical properties of TD TiN have been experimentally characterized using spectroscopy ellipsometry and theoretically investigated using both density functional theory calculations and a nonlocal Drude response model. The strong vertical confinement in TD TiN results in a consistent red shift of the optical properties and a decrease in the Drude plasma frequency in thinner films. In addition to the number of monolayers, surface oxidation and substrate properties also play a crucial role in controlling the properties of the atomically thin TiN. Most importantly, we have experimentally verified the nonlocal Drude response model, demonstrating the confinement induced thickness dependent plasma frequency in TD TiN.

Transdimensional materials can achieve remarkably large tunability of their response via free-carrier-assisted modulation due to their lower free carrier concentration compared to bulk metals and conventional thin films. Careful consideration of the thickness-dependent optical properties is required to optimize the modulation strength and device performance. Additionally, thinner films would allow control over the optical properties by adjusting the strain and lattice mismatch in the layer, facilitating a new way to engineer the optical response of the ultrathin films. While the tunable response of TCOs and 2D materials have been widely explored, studies of the TDMs' optical behavior have been limited.

Preliminary studies on TDMs show that they could exhibit strongly confined, tunable plasmons in the NIR and visible wavelengths, leading to a variety unique light-matter interactions. For example, it has been theorized that these tightly confined plasmons may enable radiative transitions in atomic-scale emitters that were considered inaccessible. Enabling access to these forbidden atomic transitions may significantly advance several different applications, including spectroscopy techniques, sensors based on forbidden transitions, as well as tunable ultrafast light generation in the near- and mid-infrared. Additionally, confined plasmons in ultra-thin structures allow for a large concentration of electromagnetic energy

which could lead to strong coupling with nearby quantum emitters. Furthermore, studies have shown TiN to have strong nonlinear properties with an increased damage threshold compared to other metal films. Due to the strong confinement observed in the atomically thin TiN, ultrathin films are expected to show an enhanced nonlinear response, which would be beneficial for all-optical devices such as ultrafast switches and frequency converters.

The realization of tunable nanophotonic devices with TDMs requires a comprehensive understanding of their plasmonic response. Appropriate models need to be developed to properly describe the evolution of the optical behavior and to design TDM-based tunable flat optical devices, or metasurfaces. Additionally, the synthesis of smooth, epitaxial, ultrathin films is critical in probing novel size effects in TDMs. As numerical modeling and material growth techniques for atomically thin materials mature, the realization of TDM-based tunable structures is expected to unlock new optical phenomena and photonic device concepts. Along with 2D materials, TDMs hold a great promise for realizing a new generation of tunable metasurfaces with quantum and nonlocal effects particularly in visible and NIR wavelength ranges.

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VITA

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