Titanium nitride (TiN) is highly attractive for plasmonics and nanophotonics applications owing to its gold-like but tunable optical properties. Its prodigious potential for plasmonics has been demonstrated on sapphire or bulk MgO. For a transformational impact, high optical quality TiN on Si is required instead, which would support the integration of nanophotonics with the complementary metal-oxide-semiconductor (CMOS) electronics. However, TiN grown on Si, even at elevated temperatures, lacks the optical quality needed, imposed by the large lattice mismatch between them. Here, a novel approach is reported wherein a thin MgO interlayer is inserted between TiN and Si. The improved crystalline quality enabled by MgO for TiN on Si(001) leads to a significant enhancement of the plasmonic figure of merit (FOM = −ε′/ε″) from 2.0 to 2.5 at telecommunication wavelength (peak FOM of 2.8), which is comparable to the widely accepted ultimate FOM obtained on bulk MgO grown under similar conditions. The TiN/MgO/Si structure enables the hybrid-plasmonic-photonic waveguide platform with sufficiently low losses, and thus long propagation lengths, for nanophotonic devices while providing additional practical advantages such as serving as a self-aligned robust etching mask. Thus, the much-anticipated potential of TiN on Si platform for CMOS compatible plasmonics is brought closer to reality.

1. Introduction

By coupling photons into collective oscillations of free electrons, plasmonics enables the emergence of novel technologies with the combined capabilities of photonics and miniaturized electronics. In the past few decades, a large variety of plasmonics-based applications have been demonstrated. These include nanolasers, interconnects, modulators, chemical- and bio-sensors, as well as light-emitting diodes and photovoltaic devices where plasmonics is used for efficiency enhancement. One of the most attractive materials alternative to noble metals that drive the plasmonics revolution, is titanium nitride (TiN), which has been investigated extensively due to its low-cost, gold-like, and tunable optical properties in the visible and near-infrared range, high thermal and chemical stability, high mechanical hardness, and bio- and complementary metal-oxide-semiconductor (CMOS) compatibilities. TiN has been widely used as a gate electrode in various CMOS devices. In the area of plasmonics, TiN-based waveguides, gyroidal metamaterials, nanohole metasurfaces, nanoantennas and use of TiN nanoparticles for solar energy conversion have been reported.

However, the majority of the demonstrations of TiN’s device potential in plasmonics have been on sapphire and bulk MgO substrates featured by their small lattice mismatch with TiN, enabling the best-performing plasmonic films. Even then, high deposition temperatures (not congruent with CMOS processes) were usually used to ensure the high structural quality of the TiN films. For example, using reactive sputtering and at a substrate temperature of 650 °C, a peak plasmonic figure of merit (FOM = −ε′/ε″) of ≈4.5 has been demonstrated for TiN films on a bulk MgO substrate. Single-crystalline, highly metallic TiN films with an electron concentration of 9.2 × 10²² cm⁻³ and a peak plasmonic FOM as high as ≈5.8 have been achieved on c-sapphire substrates by plasma-assisted molecular-beam epitaxy (PA-MBE) at a substrate temperature of 1000 °C. However, realizing the true potential of TiN-based plasmonics through integration with the CMOS electronics necessitates...
This requires the growth of high plasmonic quality TiN on Si substrates at CMOS-compatible temperatures. However, so far, only moderate plasmonic properties could be attained for TiN films grown on Si substrates using various deposition methods such as sputtering, pulsed laser deposition (PLD), and atomic layer deposition (ALD) primarily due to the associated large lattice mismatch. A relatively low resistivity of 1.5 × 10^-4 Ω cm could be achieved by PLD only at temperatures as high as 700 °C, and TiN films grown on Si at lower temperatures of 250 °C by ALD, although used to demonstrate fully CMOS-compatible plasmonic nanoantennas, exhibited weak metallic character (i.e., insufficiently large negative ε′ of -24) and much higher loss (larger ε'' of 41) compared with TiN films on MgO (ε′′ = -30 + 26) at telecommunication wavelength 1550 nm. Thus, despite significant efforts, the plasmonic quality of the heretofore reported TiN on Si does not yet satisfy the requirements for applications in integrated plasmonic devices due to a combination of high deposition temperatures or poor plasmonic performance.

In this study, we address the insufficient optical quality of TiN films on the silicon CMOS platform by the insertion of a thin (10 nm) MgO interlayer. Due to the close in-plane lattice constants of TiN (4.241 Å) and MgO (4.213 Å), this MgO interlayer significantly improves the crystalline and optical properties of TiN thin films on Si (001) substrates grown by plasma-enhanced atomic layer deposition (PE-ALD) at a moderate substrate temperature of 450 °C, as compared with direct growth of TiN on Si under the same conditions. The plasmonic FOM of TiN on Si (001) at 1550 nm enhances from 2.0 to 2.5 (peak FOM from 2.4 to 2.8) with the MgO interlayer which is comparable with the films grown on bulk MgO (001) substrates. Investigations of the material microstructure revealed that even moderate structural quality MgO interlayer gives rise to a dramatic improvement in TiN structural perfection and thus optical quality via promoting spontaneous prevailing of the cube-on-cube epitaxial growth of TiN.

This is enabled by the expansion of thermodynamically favorable (001)-oriented TiN grains winning the competition against other grain orientations due to the lowest surface energy of the TiN (001) plane. Beyond serving as a buffer layer for growth, the medium refractive index dielectric MgO layer between the metallic TiN and the high refractive index Si supports a low-loss plasmon mode in hybrid waveguide structures, resulting in dramatically improved propagation lengths. By altering the thickness of the MgO interlayer (10–100 nm), the tradeoff between propagation length and electric field enhancement can be tuned in a wide range accordingly, making the TiN/MgO/Si structure qualified for integrated CMOS-compatible nanophotonics applications. Finally, we demonstrate the added benefit of TiN as a robust etching mask to realize Si waveguides with smooth vertical sidewalls to reduce optical scattering losses which otherwise arise from the patterning process.

### 2. Results and Discussion

To illustrate the effect of the MgO interlayer, TiN films with the same thickness of ≈100 nm were grown directly on Si (001), on Si (001) with a 10 nm MgO interlayer (deposited by PA-MBE, see Experimental Section for details), and on bulk MgO (001) substrates via PE-ALD. Growth parameters including plasma exposure time, substrate temperature, and chemisorption time of the PE-ALD process were optimized to obtain TiN films with the best optical properties (see Experimental Section for additional details). We note that our TiN films grown on sapphire at low deposition temperatures of ≈450 °C have already been shown to exhibit high optical performance (peak FOM of 2.5) due to our optimized PE-ALD process involving prolonged plasma exposure and reduced chemisorption times to mitigate precursor decomposition. In regard to the structural quality, Figure 1 shows the comparison of the X-ray diffraction (XRD) 2θ–ω and φ scans of the TiN films on Si (001) with and without the MgO interlayer. The TiN (002) peak in the XRD 2θ–ω scan along the growth direction is barely apparent for the film grown directly on the Si (001) substrate (Figure 1a), indicating the low crystalline quality. However, the (002) peak intensity is significantly enhanced when the MgO interlayer is introduced (Figure 1b). The absence of other TiN diffraction peaks indicates that TiN on Si (001) with the MgO interlayer grows mainly along a single orientation. Further, the cube-on-cube growth with epitaxial relationships of TiN (001) || Si (001) and TiN [110] || Si [110] is evident from the XRD φ scans of films with the MgO interlayer showing four TiN {111} reflection peaks separated by 90° and overlapping exactly with the four Si {111} reflection peaks (Figure 1d). No diffraction peaks from TiN <111> planes were detected for the films grown directly on Si (001) (Figure 1c).

Interestingly, as shown from the scanning transmission electron microscopy (STEM) images in Figure 2, a high crystalline quality is not required for the MgO interlayer to achieve TiN thin films with substantially improved crystallinity. Figure 2c shows that the PA-MBE grown on 10 nm-thick MgO interlayer is composed of a 3 nm amorphous MgO sublayer, a 6 nm polycrystalline MgO sub-layer, and a 2 nm MgTiO or MgTiON sublayer from the Si substrate to the top. These findings are in a good agreement with the reflection high-energy electron diffraction (RHEED) evolution recorded in situ during the MBE growth (Figure S1, Supporting Information). MgO interlayer initializes in the amorphous state due to the large lattice mismatch between Si and MgO and low substrate temperature (300 °C) used during nucleation. As the growth proceeds at 680 °C, textured polycrystalline MgO with (001) preferred orientation emerges. The intermediate MgTiO or MgTiON sublayer, as evidenced by energy dispersive X-ray (EDX) spectroscopy, is a result of intermixing between the MgO and TiN layers during the ALD growth procedure (Figure S2, Supporting Information). However, this intermediate layer does not exhibit the spinel structure characteristic of Mg-containing complex oxides likely due to the relatively low ALD growth temperature. Inheriting from the MgO interlayer, the TiN film initializes in the realm of some competitions between different growth orientations for the first 20 nm. Beyond this region with competing forces, in agreement with the epitaxial relationships revealed by XRD, cube-on-cube epitaxial growth of (001)-oriented grains begins to prevail over the other orientations and eventually dominates, as confirmed by high-resolution high-angle annular dark-field (HAADF) imaging (see Figure S3, Supporting Information). The thermodynamic driving force for the predominant expansion of the (001) orientation is the lowest surface energy of the (001) plane in the TiN.
The improvement of the TiN crystalline quality with the MgO interlayer was further confirmed by the corresponding Fast Fourier Transform (FFT) pattern of the HAADF image showing mostly low-angle boundaries and the selective area diffraction (SAD) pattern taken from a 500 × 500 nm² area showing clean diffraction reflexes inherent to relatively good crystalline material containing low-angle boundaries (see Figure S3, Supporting Information).

Based on these observations, it might seem feasible to develop a low-temperature TiN nucleation route to address the lattice mismatch issue for direct TiN deposition on Si. However, the low-quality TiN nucleation layer would very likely act as an
extremely lossy “dead” layer, although the quality of the top layer is high, which would only produce usable films when grown to thicknesses >100 nm. Here, we transfer the destructive interfacial layer from the TiN/Si interface to the MgO/Si interface. An interlayer between TiN and Si, consisting of dielectric materials, regardless of its crystalline quality, does not strongly harm plasmon functionality beyond the inherent losses in the TiN layer. Instead, it provides additional opportunities and feasibility to achieve efficient plasmonic devices, which will be discussed hereinafter. It should be noted that the PA-MBE method used here is not crucial (used here for convenience) and the thin MgO interlayer may be deposited using low-temperature ALD, providing comparable crystalline quality and maintaining the CMOS process compatibility. Moreover, other oxides common to CMOS technologies, such as TiO2, SiO2, and Al2O3, could also be investigated as the interlayer between TiN and Si if the lattice mismatch issue can be alleviated. For instance, the growth of TiN/Al2O3 stack on Si for MOS capacitors has been demonstrated by several different methods such as in a single PE-ALD. Even though ALD-grown Al2O3 films on Si are typically amorphous, crystalline Al2O3 using controlled process like annealing could potentially be beneficial to improving the crystalline quality of TiN on Si.

Examining the optical properties determined via spectroscopic ellipsometry (see Figure 3), we note that the real part ($\varepsilon_r$) of the permittivity shows very weak substrate dependence for the TiN films investigated, whereas the imaginary part ($\varepsilon_i$) varies considerably with the substrate material. In general, higher crystalline quality should provide higher metallicity (more negative $\varepsilon_r$) in TiN films. However, other critical factors including stoichiometry and oxygen impurity concentration could have more significant effects on the metallicity. Therefore, TiN films with better crystalline quality had not always exhibited higher metallicity. Here, in our TiN films, the similar metallicity is speculated to be due to similar stoichiometry and oxygen impurity concentration among the samples grown on different substrates while in the same reactor under the same ALD growth conditions. In contrast, the large difference in $\varepsilon_i$ reflects that the optical losses in films on Si were significantly reduced due to the improvement in the crystallinity via the insertion of the MgO interlayer, and become comparable with those in the films grown on bulk MgO.

Figure 4a shows the comparison of the FOM, which considers the tradeoff between losses and metallicity, for TiN films on different substrates. The highest FOM was obtained for TiN grown on bulk MgO, which is consistent with the fact that bulk MgO possesses much better lattice matching to TiN than Si and higher crystalline quality compared with the MgO interlayer. Conversely, the lowest FOM curve was observed for the film grown directly on Si substrate due to the aforementioned high losses even though its metallicity is similar to that of the films grown on bulk MgO and Si with MgO interlayer. The unequivocal impact of the MgO interlayer on Si is the significant improvement of peak FOM from 2.4 to 2.8 (at $\approx$1300 nm), and the FOM at 1550 nm from 2.0 to 2.5. This improved performance, made possible by the thin MgO interlayer, nearly replicates that of TiN films grown on bulk MgO under the same conditions. As shown in Figure 4b, the use of MgO interlayer enables our TiN films to significantly outperform the plasmonic quality of other reported films grown on different substrates and by various deposition methods at CMOS compatible temperatures. More importantly, TiN films with an MgO interlayer exhibit the best performance among films grown on Si by PE-ALD and reactive sputtering at CMOS compatible temperatures, and even at higher than 600 °C, while also achieving their peak and fairly consistent performance in the telecommunications range (Figure 4a) and the solid and open connected dots in Figure 4b. It should also be mentioned that the usage of the 10 nm MgO interlayer shifts our data points to the high-performance edge of the growth temperature dependence trend (Figure 4b) for films grown on bulk MgO, even though our films were grown on a Si substrate.

In addition to the significant improvement of the TiN film quality, the TiN/MgO/Si stack inherently enables the realization of hybrid plasmonic-photonic waveguides (HPPWs), which have found versatile applications in devices such as modulators, polarization control devices, sensors, and others. As an example, Figure 5a shows the simulated electric field ($E_y$) profile of the fundamental mode in the HPPW structures with a
50 nm thick MgO interlayer, for $\lambda_0 = 1300$ nm, where the FOM peaks for TiN films on MgO. The insertion of the dielectric MgO interlayer with a medium refractive index (1.7–1.9), gives rise to the generation of a low-loss compact hybrid-plasmonic photonic mode, which does not exist in TiN/Si structures.$^{[5,54]}$ As shown in Figure 5b, when the MgO interlayer thickness is varied between 10 and 100 nm, the propagation length of the HPPWs can be tuned between 1 and 25 μm, the higher end being

![Figure 4](https://www.advancedsciencenews.com/)

**Figure 4.** a) FOM $= -\varepsilon'/\varepsilon''$ TiN thin films grown on Si (001), Si (001)/MgO, and bulk MgO (001) substrates as a function of wavelength. b) Comparison of FOMs obtained in this work with TiN films grown on sapphire, Si, and MgO substrates under deposition temperatures ranging from room temperature to 1000 °C, reported in previous studies.$^{[23,24,28,30,34,42,44,62–64]}$

![Figure 5](https://www.adpr-journal.com/)

**Figure 5.** a) Calculated model profile ($E_y$) of fundamental mode of the HPPW with a Si thickness of 340 nm, an MgO thickness of 50 nm, a TiN thickness of 100 nm, and waveguide width of 400 nm. b) Propagation lengths and field enhancement factors of the HPPW for $\lambda_0 = 1300$ nm as a function of MgO interlayer thickness assuming that the permittivity values are the same as demonstrated in this work with an MgO interlayer thickness of 10 nm. c) Comparison of the propagation length of the TiN/MgO/Si HPPW structures with the reported device lengths of plasmonic modulators in the studies by Dionne et al., Sorger et al., MacDonald et al., and Emboras et al.$^{[6,7,45,46]}$ polarization rotators in the studies by Caspers et al., Xu et al., and Kim and Qi$^{[47–49]}$ and ring resonators for applications in sensing in the studies by Butt et al., Anderson et al., and Chamanzar et al.$^{[50–52]}$ The vertical blue lines represent propagation lengths of TiN on Si dielectric-loaded waveguides using the TiN films with the permittivity values reported in the literature (deposited at 250 °C$^{[23]}$ room temperature,$^{[24]}$ and 700 °C$^{[24]}$ respectively) without the MgO interlayer and the vertical red line represents the propagation length of TiN/MgO/Si HPPW with 100 nm thick MgO interlayer.
comparable with those reported in gold-based hybrid waveguides.\textsuperscript{[55]} Moreover, increasing the MgO thickness from 10 to 100 nm decreases the electric field enhancement factor from 6.9 to 1.3 as expected. This is because a smaller gap size leads to a stronger optical coupling between the plasmonic and photonic modes, providing the ability to optimize electric field enhancement and propagation loss by simply altering the thickness of the MgO interlayer.

The practical significance of the propagation length afforded by the TiN/MgO/Si stack is clearly shown in Figure 5c, when it is compared with the device lengths of some recently reported compact plasmonic devices including electro-optic modulators, polarization rotators, and ring resonators (circumferences are used as the device lengths) for sensing applications using common plasmonic metals such as Au, Al, Ag, and Cu. Device lengths for all of these demonstrations lie in the range from a few micrometers to a few tens of micrometers. Without an MgO interlayer, the losses in dielectric-loaded waveguides on the TiN/Si platform would make the realization of such applications extremely challenging when compared with those based on Au and Ag. As shown by the blue vertical lines, propagation lengths of TiN on Si dielectric-loaded waveguides without an MgO interlayer are all below 1 μm (using the permittivity values reported in the literature for films deposited at room temperature\textsuperscript{[34]} 250,\textsuperscript{[23]} and 700 °C\textsuperscript{[24]}), translating to more than 8 dB μm\textsuperscript{-1} of propagation loss. In contrast, due to the significantly improved plasmonic performance, the as-grown TiN/MgO/Si HPPWs can provide sufficiently long propagation lengths for all of the applications listed.

In addition to the propagation loss, optical scattering losses arising from the edge roughness produced during fabrication could significantly undermine the device performance or necessitate multiple complex fabrication steps to eliminate.\textsuperscript{[56]} Compared with metals like Au, TiN is significantly easier to process and can provide high-quality vertical edges due to its robustness and high etching selectivity. As an example, the cross-sectional and plan-view scanning electron microscopy (SEM) images of step-etch profiles in TiN/MgO/Si and Au/Si structures obtained using chlorine chemistry-based reactive ion etching (RIE) of TiN and Au, followed by fluoride-based RIE of Si are compared in Figure 6. Due to its crystalline nature and ease of etching in chlorine chemistry, a relatively vertical sidewall with a straight edge was achieved for the TiN/MgO/Si structure. In contrast, a highly sloped sidewall with a much higher edge roughness was obtained for the Au/Si structure. Another significant advantage of TiN is its ability to serve as a self-aligned hard mask for subsequent etching steps without any considerable physical or chemical etching. Therefore, it helps to both reduce the scattering loss and simplify fabrication processes for integrated nanophotonic structures. Although Au is also not reactive, its softness limits its ability to be used as a hard-mask, thereby requiring additional lithography steps, a separate hard mask, or an extremely thick resist to effectively pattern. As a result, our platform not only enables improved plasmonic performance of TiN with readily access to a CMOS compatible HPPW structure, but also provides inherent advantages in simplifying high-quality device fabrication and processing.

![Figure 6. Cross-sectional and top-view SEM etching profiles of a,b) Au/Si and c,d) TiN/MgO/Si structures using chlorine chemistry-based recipes for TiN and Au etching followed by fluoride-based recipe for Si etching. A vertical sidewall with a straight edge was achieved for the TiN/MgO/Si structure, whereas an angled sidewall with large-scale rough features observed for the Au/Si structure.](image-url)
3. Conclusion

We have demonstrated the significant impact of an MgO nucleation interlayer to the plasmonic quality and device functionality of the TiN on Si platform for CMOS compatible plasmonics and nanophotonics. Using a 10 nm moderately crystalline MgO interlayer, the overgrown TiN films are shown to evolve from multiple oriented to thermodynamically favorable, (001)-oriented single crystal, thereby producing a high plasmonic FOM of 2.5 at 1550 nm and peak FOM of 2.8 due to the reduction of optical losses. The result is the translation of TiN to the bulk-MgO growth curve on a Si platform. Moreover, this tendency illustrates that under the PE-ALD growth conditions, a highly crystalline interlayer is not required to improve performance, which thereby opens a potential for scalable low-temperature deposition processes for TiN on Si. We have also shown that, in addition to acting as a nucleation layer, such a medium refractive index MgO interlayer between the metallic TiN and the high-index Si inherently supports a compact low-loss hybrid plasmonic mode and provides key practical processing benefits as a self-aligned etch mask for optical waveguides, thereby providing a framework to realize efficient CMOS-compatible plasmonic devices on Si.

4. Experimental Section

MgO Interlayer Growth: Growth of thin MgO interlayers on Si (001) substrates was carried out using PA-MBE equipped with a RHEED system so that the evolution of growth can be in situ monitored. A Knudsen cell was used to evaporate Mg, and a radio-frequency plasma source operating at 400 W was used as the source of reactive oxygen. Before loading into the MBE system, Si substrates were treated by a chemical cleaning process, which includes degreasing, boiling in dilute HCl and H₂O₂ solution to remove metal ions, followed by removing the oxide layer in dilute HF, rinsing in deionized water, and blow-drying with nitrogen. After in situ degassing at 650 °C for 10 min, the substrate temperature was reduced to 300 °C for the deposition of a 2–3 nm MgO nucleation layer preceded by a 30 s Mg pre-exposure step to prevent oxidation of the Si substrate. Then the substrate temperature was raised, and a high-temperature MgO layer was deposited at 680 °C for the subsequent TiN growth. The growth rate of the MgO layer was about 0.7 nm min⁻¹. As reported in the literature, high-quality MgO thin films could be realized by low-temperature processes such as ALD and electron beam evaporation, suitable for future development of fully CMOS compatible films for integrated devices.

TiN Growth: As a scalable and conformal technique for industrial-scale operation, a low-temperature plasma-enhanced atomic layer deposition (LT-PE-ALD) system was used for the growth of TiN thin films on the MgO/Si composite described earlier. Tetakis (dimethylamino) titanium (IV) (TDMAT) and nitrogen plasma were used as the Ti and N precursors, respectively. Each cycle of ALD consisted of a pulse of TDMAT on to the heated substrate followed by exposure to N₂ plasma. Deposition parameters of a plasma exposure time of 25 s, a chemisorption time of 0.5 s, and a substrate temperature of 450 °C were used based on previous optimization routines to obtain the material with the best optical properties. For a comparative study, the simultaneous growth of TiN directly on Si (001) without an MgO interlayer, and on bulk MgO (001) substrates was also carried out. The growth rate of the TiN films was about 1.3 Å per cycle, independent of the substrate material.

Reactive Ion Etching: The TiN was etched in a Samco inductively coupled plasma (ICP) etching system (model: RIE-101 iPH) with photoresist as the mask. Chlorine chemistry-based RIE had been demonstrated to couple plasma and etch TiN with high selectivity to Si. Chlorine chemistry-based RIE had been demonstrated to couple plasma and etch TiN with high selectivity to Si. As reported in the literature, high-quality MgO thin films could be realized by low-temperature processes such as ALD and electron beam evaporation, suitable for future development of fully CMOS compatible films for integrated devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All data are available from the corresponding author upon reasonable request.
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