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Facile integration of electro-optic SiO₂/ITO heterointerfaces in MIS structures for CMOS-compatible plasmonic waveguide modulation

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Abstract

By taking advantage of the absence of diffraction limit restrictions in plasmonic structures, strong modal confinement is made possible, paving the way for improved optical processes and miniaturized photonic circuit integration. Indium tin oxide (ITO) has emerged as a promising plasmonic material that serves as a relatively lowcarrier density Drude metal by its electro-optic tunability and versatility as an integrative oxide. We herein demonstrate the facile integration of SiO₂/ITO heterointerfaces into metal-insulator-semiconductor (MIS) electrooptic structures. The first MIS device employs a SiO₂/ITO heterostructure grown on thin polycrystalline titanium nitride (poly-TiN) and capped at the ITO side with thin aluminum (AI) film contact electrode. The TiN interlayer acts as a bottom electrode, forming a metal-insulator-semiconductor-metal (MISM) heterojunction device, and grows directly on (100)-oriented silicon (Si). This MISM device enables one to examine the electrical properties of semiconductive ITO layers. The second MIS device incorporates a semiconductive ITO layer with a SiO₂ dielectric spacer implemented on a silicon-on-insulator (SOI) platform, forming a graded-index coupled hybrid plasmonic waveguide (CHPW) modulator. This device architecture represents a crucial step towards realizing plasmonic modulation using oxide materials. The CHPW device performance presented herein provides a proof-of-concept that demonstrates the advantages offered by such device topology to perform optical modulation via charge carrier dispersion. The graded-index CHPW can be dynamically reconfigured for amplitude, phase, or 4-quadrature amplitude modulation utilizing a triode-like biasing strategy. It exhibited extinction ratio (ER) and insertion loss (IL) levels of around 1 dB/µm and 0.128 dB/µm, respectively, for a 10 µm waveguide length.

Keywords: Indium tin oxide (ITO), Modulators, Oxide semiconductors, Plasmonics, Telecom frequency, Titanium nitride (TiN)

Introduction

While the practical employment of plasmonic components is usually hindered by the intrinsic absorption of metals, this issue turns progressively severe with field confinement¹⁻⁴. Accordingly, plasmonic resonators for

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instance typically exhibit a limited Purcell factor (i.e., quality factor [Q] to effective mode volume $[V_{\text{eff}}]$ ratio $[Q/V_{\text{eff}}]$), which impedes their potential employment in the fields of nonlinear optics, quantum optics, signal processing, and sensing^{5–8}. However, in slot waveguides such as the one investigated herein, optimizing and reducing optical and electrical losses is the main interest⁹. Given that plasmonic mode confinement within a small

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width contributes to the reduction in optical mode area and therefore enhances light-matter interaction, higher ohmic losses causing surface plasmon polariton (SPP) decays are anticipated because of reduced plasmonic waveguide propagation lengths, which is not a desirable attribute in light-modulation devices¹⁰. Furthermore, an accurate assessment of modulator performance is crucial to optimize the design of device contact layers. This necessitates a thorough investigation of carrier density distribution in order to understand how they can be efficiently dispersed within a semiconductor layer upon applying a bias voltage, as well as be transported between, for example, metal contacts and a silicon (Si) layer. The results of this investigation can find application in several fields, specifically in Si-integrated modulated light sources, where optical modulators based on metal-oxide-semiconductor (MOS) architectures can achieve fast switching characteristics with the light emitter lifetime being controllable via the capacitor discharge time^{11,12}.

As can be found in the literature, the use of noble metals such as silver (Ag) and gold (Au) have dominated the field of plasmon-electronics because of their high free electron density and conductivity levels, which are in the order of 10^{22} cm⁻³ and 10^7 S/m, respectively¹³. However, given the large optical losses exhibited by these metals at long wavelengths, their integration in plasmonic lightmodulation devices operating within the near-infrared (NIR) regime is not favorable¹⁴. On the other hand, indium tin oxide (ITO) is a promising suitable material for integration in NIR plasmonic modulators. Its nature as a semiconductor layer facilitates the tunability of its optical properties, which can be induced by modifying the and doping concentration¹⁵. deposition conditions Moreover, it has been theoretically predicted that the analysis of waveguides incorporating ITO as a semiconductor using a uniform accumulation layer (UAL) model is not rigorous, especially when the driving voltage necessary for tuning ITO is sufficiently high that uncertainty in determining the accumulation layer thickness is warranted¹⁶⁻²⁴. This becomes clear when the epsilon-near-zero (ENZ) regime properties^{25,26} are revealed, as shown using the rigorous graded-index layer (GIL) model analysis which shows that such cannot be predicted in those based on the UAL model.

Plasmon-electronics exploit the extreme confinement of light to achieve efficient amplitude and phase modulation on the scale of a few micrometers²⁷. The facile integration with electrical contacts entails even further device miniaturization opportunities and higher energy efficiency²⁸. However, fast yet small-scale plasmonic modulators generally suffer from large ON-state losses in

the order of 1 dB/ μ m²⁹. As a result of poor coupling efficiency with the desired plasmonic modes, modulator insertion loss (IL) levels can reach 10 dB²⁹⁻³¹. Recently, plasmonic modulators incorporating transparent conducting oxides such as ITO have received considerable interest, as, under the assumption of uniform carrier accumulation, unity-order refractive index changes have been observed in ITO thin films under gate biases²⁴. Although such a strong electro-optic effect is theoretically promising for reducing modulator footprint, the index change can only occur within a locally induced accumulation layer that is a few nanometers in thickness. Such minuscule overlap between the accumulation layer and the plasmonic modal crosssection necessitates an extended device length to obtain reasonable extinction ratio (ER) levels, which inevitably leads back to substantial IL³². Moreover, plasmonic modulator designs proposed to date have largely focused on amplitude modulation^{33,34}. As such, there is still a need for a compact, low-power modulator design that can avert the strict ER-IL trade-off, better exploit the tunable properties of thin-film optical materials such as ITO, and support different modulation types.

In this work, the facile integration of SiO₂/ITO heterointerfaces into metal-insulator-semiconductor (MIS) electro-optic structures is presented as shown in Fig. 1. Using processes that are fully compatible with complementary metal-oxide-semiconductor (CMOS) front-end-of-line (FEOL) requirements, a Si-integrated MIS device that employs a SiO₂/ITO heterointerface along with a polycrystalline titanium nitride (poly-TiN) conductive template³⁵, was fabricated and characterized. The poly-TiN template acted as a bottom electrode, realizing a metal-insulator-semiconductor-metal (MISM) heterojunction capacitor that is capped at the top with aluminum (Al), and was directly grown on (100)-oriented Si substrate. Because of lattice mismatches, epitaxial monocrystalline films exhibit relatively higher strain levels that develop during high-temperature growth processes. Polycrystalline films on the other hand develop strained lattices that come only from surface tension effects and differences in thermal expansion coefficients. Furthermore, poly-TiN acts as a conductive ceramic interlayer with antidiffusion and refractory metallic properties while offering excellent thermal conductivity^{36,37}. The realization of this MISM device allows for the close examination of the ENZ properties of semiconductive ITO layers ($n \approx 6.3 \times 10^{20}$ cm⁻³) integrated in oxide–semiconductor heterojunctions. We also demonstrate another MIS device incorporating a semiconductive ITO layer with a SiO₂ dielectric spacer: A coupled hybrid plasmonic waveguide (CHPW) modulator integrated on a silicon-on-insulator (SOI) platform.

Experimental validation of the GIL model in the ITO-based MISM structure is presented to predict the accumulation layer width upon biasing. The graded-index layer CHPW modulator can be dynamically reconfigured for amplitude, phase, or 4-quadrature amplitude modulation utilizing a triode-like biasing strategy. A 10-µm-long CHPW modulator demonstrated ER and IL levels of around 1 dB/µm and 0.128 dB/µm, respectively. Our findings concerning the change in carrier distribution behavior in the ITO layer with varying gate voltage were observed in the fabricated MISM heterojunction device. This laid the foundations for minimal electrical losses by exploiting an optimized metal contact layer design. We note that related CHPW modulator results were exhibited in a previous publication⁶. However, in this current study, we report comprehensive materials-based electrical analysis investigated through the MISM structure and analyze the carrier dispersion characteristics within the CHPW using the GIL model. Utilizing this model, accurate optical simulation results are now revealed, demonstrating significantly lower variations in the CHPW effective refractive index and propagation loss (PL) levels with bias application, given the ENZ-regime charge carrier concentration level within our ITO thin film¹⁶. Moreover, the balance between ER and IL levels suggests a strict trade-off when designing plasmon-electronic propagatingwave modulators. This, of course, implies a substantial compromise in device footprint and energy intake, which distinguishes our work presented here because we show that CHPW-based modulator architectures can alleviate the trade-off above to a considerable extent. The extracted and analyzed wavelength-dependent CHPW attributes exhibited here can be used for wavelength division multiplexing³⁸.

ITO's carrier dispersion properties are the key mechanism behind the operation of the CHPW modulator presented in this work. ITO is a wide-bandgap ($E_g > 3 \text{ eV}$) oxide semiconductor that can be highly conductive since it can be degenerately doped (n-type) and can exhibit free carrier concentrations of up to 10²² cm⁻³. On the other hand, the carrier density in our case (i.e., in the order of 10^{20} cm⁻³, obtained by increasing the level of O₂ vacancies in the film) is low enough such that the real part of its permittivity is small compared to noble metals and typical dielectrics. This leads to a substantial enhancement of the optical field across it once it is placed inside our CHPW structure with an adjacent high-index Si layer, as required by the continuity of the displacement field. By biasing our SiO₂/ITO-based MISMs, electron accumulation/depletion layers are formed at the SiO₂/ITO interfaces that lead to carrier-induced variations in ITO's permittivity and therefore modulate the intensity of the propagating longrange transverse magnetic (TM_{LR}) supermode. Intuitively, the electrostatics of MISMs are heavily governed by the properties of the embedded oxide layer. A thinner oxide layer can enable sufficient carrier accumulation at smaller voltages and thus minimizes the modulator's energy consumption. However, the electric field breakdown of the oxide dictates the upper bound for capacitive accumulation.

As a material for contact electrodes, ITO acts as a lowcarrier-density Drude metal³⁹⁻⁴³. It is imperative to note that a non-degenerate ITO thin film behaves as a semiconductor with relatively low electrical resistivity (in the order of 10^{-4} $\Omega \cdot cm$) and high optical transmittance (> 80%) within the visible-light spectrum 44,45, even when unbiased. But once it is biased within the ENZ zone as shown in Fig. 2 and Fig. 3, it acts as a plasmonic material. A depletion region is created in ITO when a static electric field is applied to drive back mobile electrons near the surface at the ITO/dielectric interface, where variations in carrier concentration affects several physical attributes such as its conductivity and dielectric constant^{16, 46-48}. However, because Ag and Au have relatively high electron densities, the depletion layers formed in such materials are ångströmscale. Therefore, the effects of local variations in carrier density and conduction of a noble metal structure tend to be negligible and dominated by other events, whereas ITO carrier concentrations are naturally lower than those of noble metals; thus, ITO films are relatively easier to deplete^{22,39,41,49}. The average Fermi wavelength ($\lambda_{\rm F}$) scales inversely with the cube root of the electron density $n_{\rm e}$ as $\lambda_{\rm F} = 2\pi/(k_{\rm F}) = 2\pi/\sqrt[3]{3\pi^2 n_{\rm e}}$, where $k_{\rm F}$ is the Fermi wave vector. ITO structures with a typical $\lambda_{\rm F}$ of approximately 5 nm are more prone to quantum effects than those from noble metals with a $\lambda_{\rm F}$ of about 0.5 nm³⁹.

Fig. 1a depicts a schematic illustration of the first MIS structure under investigation, namely the Si-integrated Al/ITO/SiO₂/TiN MISM. Fig. 1b shows a schematic illustration of the multilayer CHPW structure based on the same ITO/SiO₂ heterojunction housed directly on an SOI substrate. Application of an external voltage across a SiO₂/ITO interface causes charge carriers to be injected through the metal contacts, forming a voltage-induced accumulation layer, rendering the device capable of optical modulation by exploiting the ENZ effect once carrier accumulation is sufficient. Such a plasmonic waveguide design can alleviate the loss-confinement trade-off, as demonstrated previously by our group⁶. This waveguide was built by linking a Schottky junction and MIS stack through a mutual metal layer⁷. From an optical point of view, the structure compounds the advantages of coupled⁵⁰ and hybrid⁵¹ plasmonic waveguide modes, simultaneously



accomplishing long-range propagation and nanoscale modal confinement. The Supplementary Information document provides a theoretical overview of ITO's ENZ properties.

The Si-integrated Al/ITO/SiO₂/TiN MISM demonstrates the facile formation of a SiO₂/ITO heterojunction on a conductive ceramic interlayer formed via high-temperature growth of SiO₂ at 330 °C using plasma-enhanced chemical vapor deposition (PECVD), and magnetron sputtering of ITO at room temperature. This approach utilized the effective refractory, anti-diffusion, and electrical and thermal conductivity properties of poly-TiN to grow dense, high-quality SiO₂ layers at high temperatures, followed by ITO layers, to form vertically integrated MIS heterostructures capped with e-beam evaporated Al layers. These simplistic MIS structures were then used to investigate the carrier dispersion properties of the semiconductive ITO layer and their effect on the structures' optical performance upon bias application. This approach represents a neat and comprehensive investigation of the MIS structure before linking it to another (i.e., a-Si/Al) to form a Schottky junction comprising the multilayer CHPW by simply sputtering amorphous Si (a-Si) at room temperature. This scheme establishes the facile manner via which practical CHPW devices can be designed and fabricated.

Aside from being used as semiconductor layers for plasmonic applications, as in our case, ITO bulk films are widely used as transparent electrodes in a multitude of optoelectronic devices, but they have their shortcomings. These include high production cost given the scarcity of indium (In) combined with the need for vacuum deposition and several post-processing steps^{52–55}; mechanical brittleness inherent in oxides because of crack formation upon mechanical bending, which causes reduced electrical conductivity^{56–58}; poor adhesion to polymeric and organic materials, rendering the integration of ITO in flexible electronics infeasible^{59–61}; and long-term durability concerns owing to its thermodynamic instability at potentials below 0.6 V and chemical degradation caused by the intermediate formation of secondary species concentrates such as In, tin(II) oxide (SnO), and tin (Sn)^{62,63}.

CHPW numerical simulations

Our CHPW design effectively addresses the lossconfinement tradeoff by supporting supermodes formed through the superposition of an SPP mode and a hybrid plasmonic waveguide (HPW) coupled via a thin metal film. Light-matter interaction on two types of plasmonic interfaces-metal with high-index dielectric and metal with low-index dielectric-is suggested by combining dissimilar modes in one structure. The latter confines modal energy within the dielectric layer, allowing for more powerful linear and nonlinear processes. The modal analysis of the CHPW structure at $\lambda = 1550$ nm was performed using the Lumerical Finite-Difference Eigenmode (FDE) solver, with the perfectly matched layer boundary settings and mesh set to a maximum value of 0.001 µm. The FDE solver calculates the modal spatial profile and frequency dependence by solving Maxwell's equations on a crosssection mesh of the waveguide. Table 1 summarizes the material parameters used in CHPW simulations.

The plasmonic mode profiles were calculated based on the carrier distribution in the ITO layer. The local permittivity in the ITO layer will determine the modal shape. However, permittivity is a function of carrier distribution. It can be calculated once the carrier distribution is determined. The optical properties of ITO, or more precisely, its permittivity, change as a function of the carrier distribution. The Drude model can describe the relation between the carrier distribution and permittivity as described by the following relation

$$\varepsilon_{\rm ITO}(z,\omega) = \varepsilon_{\infty} - \frac{\omega_{\rm p}^2(z)}{\omega^2 - j\gamma\omega} \tag{1}$$

described in the Supplementary Information document, which sufficiently describes the relative permittivity at NIR wavelengths. The plasma frequency ω_p is directly linked to the carrier density *n* via the following relation

Layer	DC permittivity	Work function (eV)	Bandgap (eV)	Electron mobility (cm²/(V·s))	Hole mobility (cm²/(V·s))	Refractive index
Si	11.90	4.61	1.10	1471	470.50	3.48
ITO	3.90	5.40	2.60	12.10	_	2.14 ± <i>j</i> 0.14
SiO_2	3.90	_	-	-	_	1.47
Al	-	4.28	-	-	_	2.73
a-Si	-	-	-	-	-	3.73

Table 1 Summary of material parameters used in CHPW simulations

$$\omega_{\rm p} = \sqrt{q^2 n / (\varepsilon_0 m^*)} \tag{2}$$

described in the Supplementary Information document. The parameters of the Drude model depend on the ITO material properties where $\gamma = 1.8 \times 10^{14}$ rad/s at $\lambda = 1550$ nm and an effective electron mass m^* of $0.35m_0$, where $m_0 \approx 9.109 \times 10^{-31}$ kg is the rest mass of an electron.

We used Lumerical's Charge Transport (CHARGE) solver to calculate the spatial depletion and accumulation of electrons in the ITO layer across the SiO₂/ITO interface when the bias voltage was varied between -10 V and 25 V. Theoretical information about the used algorithm is presented in the Supplementary Information document. The plots were obtained by calculating the carrier distributions at the SiO₂/ITO interface at different voltage levels. These depletion and accumulation processes change the permittivity of ITO thin films in compliance with the Drude model, which opens gateways for realizing optical modulation. Once the change in permittivity reaches the ENZ regime from the modulation, it dramatically changes the absorption of ITO.

The density of charge carriers at different voltage levels obtained from the CHARGE solver was transported to Lumerical FDE MODE solver through an index perturbation (*np* density) grid, which tuned the optical constant of ITO, leading to a change in the complex effective refractive index of the mode propagating in the CHPW structure. The plots exhibit changes in the real and imaginary parts of the effective refractive index with varying applied voltage. ER and the ON-state PL are parameters that can be used to quantify an optical modulator's performance. An effective modulator has high ER and low PL levels. The complex effective refractive index us to describe the ER and PL for a given voltage bias. The PL was calculated using⁶⁴

$$PL [dB/\mu m] = 10 \log(e \cdot \alpha)$$
(3)

where $e = \sum_{n=0}^{\infty} 1/n!$ is the base of natural logarithms (Euler's number) and α is the absorption coefficient, which can be determined as follows

$$\alpha = \frac{4\pi k_{\rm eff}}{\lambda} \tag{4}$$

where $k_{\rm eff}$ is the effective extinction coefficient (i.e., the imaginary part of the effective refractive index). The ER in dB/µm is the difference between the absorption coefficient of the transmitting ON-state ($\alpha_{\rm ON}$) and absorbing OFF-state ($\alpha_{\rm OFF}$), i.e.,

$$ER = 10\log(e(\alpha_{OFF} - \alpha_{ON}))$$
(5)

Fig. 2 displays the observed changes in PL levels and the real and imaginary parts of the effective refractive index (Fig. 2a, b, respectively) of the CHPW waveguide varying applied voltage using the GIL model for an ITO with $n = 6.3 \times 10^{20}$ cm⁻³. These plots demonstrate significantly lower variations in the optical constants given the nature of our ITO layer with a doping concentration $n = 6.3 \times 10^{20}$ cm⁻³ being within the ENZ regime.

Fig. 3 plots the observed changes in carrier density and electric field (Fig. 3a, b, respectively) levels across the CHPW waveguide with varying voltage using the GIL model. In Fig. 3a, we observe a depletion of free electrons after applying a negative bias at the insulator side. On the other hand, an accumulation of free electrons was achieved by applying a positive bias at the same terminal. This accumulation of electrons led to higher current flow levels that gradually increased with positive bias application. As one can observe in Fig. 3b, the magnitude of the electric field across the SiO₂ layer is linearly dependent on the applied bias and is directly influenced by carrier accumulation/depletion at the SiO₂/ITO interface, demonstrating that the ITO's carrier dispersion properties are the key mechanism behind the operation of the CHPW modulator.

Device fabrication

Si-integrated AI/ITO/SiO₂/TiN MISM

Fig. 4 depicts a schematic illustration of the TiN/Siintegrated Al/ITO/SiO₂ MISM fabrication process. A commercially procured (100)-oriented single-crystalline Si substrate that is 20 mm \times 20 mm \times 0.5 mm in size was



levels, which inevitably leads back to substantial IL levels.

used as a growth platform for the Al/ITO/SiO₂/poly-TiN heterostructure. The Si substrate was ultrasonically cleaned in a bath of acetone and isopropyl alcohol (IPA, Fig. 4a. It was then introduced into a magnetron reactive sputtering processing chamber for depositing a 100-nm-thick poly-TiN template as depicted in Fig. 4b. The substrate was first degassed for 30 min at 350 °C, etched for 30 min at 350 °C in a 50 W plasma generated in a 5 mTorr argon (Ar) background to activate the surface, and further annealed in a vacuum at 700 °C for 2 hours to thermally sublimate native SiO₂.

The poly-TiN films were deposited at a substrate temperature and bias of 700 °C and -120 V, respectively, using DC magnetron reactive sputtering of one Ti target operated at a power of 90 W in an Ar-nitrogen (N₂) reactive atmosphere of 5 mTorr total pressure fed by 27 sccm of Ar and 2.2 sccm of N₂ flow rates. The poly-TiN deposition rate was about 1.15 nm per min. A poly-TiN thickness of 100 nm corresponds to a deposition duration



of about 75 min, high enough to ensure adequate electrical conductivity because the resistivity of thin metallic films with thicknesses lower than 100 nm is dominated by interface scattering effects³⁶. Fig. 5a displays a grazing incidence X-ray diffraction (GIXRD) measurement performed on the grown poly-TiN layer with indexed plane peaks, confirming the polycrystalline nature of the grown thin film. Atomic force microscopy (AFM) imaging results of the grown poly-TiN film show a measured RMS roughness of approximately 1.12 nm (refer to the Supplementary Information document).

Then, as shown in Fig. 4c, an approximately 20-nmthick SiO₂ was deposited using PECVD at 330 °C, with 170 sccm SiH₄/N₂ and 710 sccm N₂O gas flow rates and 20 W radiofrequency (RF) forward power for around 16 seconds, forming the oxide dielectric layer of the MISM. AFM imaging results of the deposited SiO₂ film show a measured RMS roughness of approximately 1.36 nm (refer to the Supplementary Information document). To define the regions where Al/ITO junctions were to be formed, a



Fig. 4 TiN/Si-integrated MISM—Fabrication process: **a** Si wafer preparation; **b** magnetron sputtering of polycrystalline TiN; **c** SiO₂ dielectric deposition; **d** photoresist spin coating, exposure, and development; **e** magnetron sputtering of ITO; **f** electron beam evaporation of Al; **g** ITO and Al lift-off; and **h** selective dry plasma etching of SiO₂.



of the grown TiN layer. **b** IV measurements performed across two points on the grown TiN layer after dry SiO₂ etching with 300 μ m separation distance.

bilayer lift-off process was employed whereby two PMGI SF7 and Shipley S1811 photoresist layers with total thicknesses of around 800 nm and 1 μ m were successively spin-coated at 1500 and 5000 rpm, respectively, to ensure a smooth lift-off process of the ITO (~20 nm) and Al (~250 nm) relatively thick film stack. The resultant pattern

is shown in Fig. 4d. An approximately 20-nm-thick ITO layer was then sputtered using RF magnetron sputtering of one ITO target (90% In_2O_3 and 10% SnO_2 w/w%) at 150 W for 270 seconds with 50 sccm Ar and 0.50-0.80 sccm oxygen (O₂) gas flows (F_{O_2}) at room temperature (Fig. 4e). This was followed by depositing a 250-nm-thick Al layer using an e-beam evaporator (Fig. 4f). As depicted in Fig. 4g, the deposited ITO/Al layers were lifted-off overnight in a Remover PG solution, followed by a oneminute Remover PG bath and a one-minute IPA bath, both at room temperature. The sample was then rinsed in DI water. Finally, the exposed area of the SiO₂ layer was dryetched at 20 °C using 38 sccm Ar and 12 sccm CHF₃ gas flows for 35 seconds to render accessible the poly-TiN bottom electrode for electrical measurements (Fig. 4h). Fig. 5b displays current-voltage (IV) measurements performed across two points on the grown poly-TiN layer (300 μ m apart) after SiO₂ dry etching. These measurements show that the poly-TiN layer is conductive with a series resistance of around 26.20 Ω , confirming the complete removal of the SiO₂ film after the dry plasma etch process.

CHPW modulator

Fig. 6 depicts a schematic illustration of the CHPW modulator fabrication process. This multi-layer-structure (i.e., $a-Si/Al/SiO_2/ITO$) CHPW device comprises a high-index bottom dielectric layer, a low-index dielectric spacer, a metal layer, a high-index top dielectric layer, and an ITO layer that is incorporated as part of the spacer layer. For integration with Si photonics, a Soitec Unibond SOI wafer was chosen as the device platform, which has a 220-nm-thick single-crystalline Si layer serving as the bottom high-index layer. SiO₂ and Al, respectively, were selected as the spacer and metal layers to ensure compatibility with CMOS processes. The top high-index layer was chosen to



nm-thick SiO₂; **f** e-beam evaporation of Al; **g** magnetron sputtering of 200-nm-thick a-Si; **h** a-Si trench formation using DRIE; **i** formation of Si nanowires and CHPW components by etching through the entire waveguide stack; **j** selective-area etching of the a-Si layer; **k** sputtering and subsequent lift-off of 200-nm-thick Al contact pads. Inset: Electron microscopy imaging—Bird's-eye SEM view of a fabricated 10- μ m long SiO₂/ITO CHPW modulator.

be a 200-nm-thick a-Si deposited at room temperature to avoid Al diffusion or oxide formation at higher deposition temperatures. Based on our previous analysis⁶⁵, the width of the CHPW modulator was fixed at around 200 nm to minimize IL levels. Light is coupled in and out of the active CHPW components using 775 nm wide Si nanowires. Contact pads for the modulator were designed with 100 μm-wide pitch to match that of a commercial high-speed RF probe.

To fabricate the CHPW, a bottom-up fabrication approach was implemented via the lift-off technique because of the overall higher reproducibility and device yield. The stacked layers were deposited only at the desired regions, eliminating inconsistencies from wet etching processes. The CHPW fabrication process started with SOI substrate preparation Figs. 6a–c. As depicted in Fig. 6a, the substrate was cleaned using a piranha solution ([4:1] $H_2SO_4:H_2O_2$ for 10 minutes), a buffered oxide etchant (BOE, for 10 seconds), and an RCA solution ([6:1:1] $H_2O:HCI:H_2O_2$ for 10 minutes at 60 °C). The SOI wafers

were cleaned using piranha, BOE, and RCA solutions to remove metals and organic contamination to which nanoscale waveguide operation can be sensitive. The substrate was then passivated with a sputtered 5-nm-thick SiO₂ layer (at 3 mTorr working pressure, 300 W magnetron power, and 30 sccm Ar flow rate for 72 seconds at room temperature) as shown in Fig. 6b before sputtered 60-nm-thick tungsten (W) markers (at 3 mTorr working pressure, 200 W magnetron power, and 30 sccm Ar flow rate for 720 seconds at room temperature) were patterned via a lift-off process (using a patterned MMA/PMMA resist) as shown in Fig. 6c. After that, a 10-nm-thick ITO layer was sputtered to create the electro-optic layer in the modulator device region (Fig. 6d), followed by an e-beam evaporation of 20-nm-thick SiO₂ layer (Fig. 6e) at room temperature. E-beam evaporated SiO₂ was used instead of PECVD in the case of CHPW fabrication, given that it follows ITO deposition and ITO electro-optic properties are sensitive to high-temperature processing. This SiO₂ layer would serve as the low-index spacer for the CHPW.

A 10-nm-thick Al layer was then e-beam evaporated (Fig. 6f) to form the metal layer for the CHPW device and serve as an etch mask for the ITO thin film. To obtain the functional CHPW device, the areas where the input and output Si nanowires are located on the sputtered a-Si layer (Fig. 6g) were selectively patterned and etched (Fig. 6h) using deep reactive-ion etching (DRIE) to expose the regions where the input/output Si nanowires will eventually be located. The patterning was performed using an electron beam lithography tool to achieve the desired high-resolution features (100 kV accelerating voltage and beam current of 50 nA and 1 nA for the bulk and sleeve regions, respectively). The Si nanowires and CHPW components were created by etching through the entire waveguide stack (Fig. 6i), while the a-Si layer was etched afterward to reveal regions where device contacts will be made (Fig. 6j). Finally, as shown in Fig. 6k, 200-nm-thick Al pads were sputtered and lifted off to create the contact layers.

A bird's-eye view scanning electron microscopy (SEM) image of a fabricated CHPW modulator is shown in the inset of Fig. 6. Contacts were formed by extending the Al and ITO layers away from the waveguide region via fingers that are 475 nm-wide and separated by 2 μ m gaps. This was to ensure minimal disturbance to the optical mode. The anode (S) and cathodes (G), consisting of 200-nm-thick Al layers, are sputtered onto the extended Al and ITO regions. To facilitate probing, the area of the Al pads is larger than that of the existent contact region. Under an external bias, carriers are injected through the contacts, and the formation of a voltage-induced accumulation layer as the SiO₂/ITO interface enables optical modulation.

Electrical characterization

MISM CV characterization

At the waveguide region, the Al/SiO₂/ITO stack is equivalent to an MIS described by a capacitance $C_{\rm MIS}$ and a parallel (or shunt) resistance R_{MIS} . Fig. 7 displays the capacitance-voltage (CV) measurements that were performed on circular MISMs with a radius size of 100 µm. While the area-normalized capacitance values shown in Fig. 7 are reported for CV measurements performed with a small-signal frequency component of 1 MHz, the Supplementary Information document provides CV measurements performed with small-signal frequency components of 10 kHz and 100 kHz. The electrical probe station used to measure this structure is described in the materials and methods section under electronic properties. To have a properly functioning MISM device, the phase angle (θ) between the current through and voltage across



Fig. 7 MISM CV plots —Frequency response curves of fabricated SiO₂/ITO MISMs with different n_{ITO} levels as functions of bias voltage.

the device must be around -90° C, implying that there is no significant influence of series resistance (R_s) on the measured impedance (Z) and hence it is entirely imaginary considering the following expression for a capacitor impedance

$$Z = R_{\rm s} + \frac{1}{j\omega C} \tag{6}$$

where $j = \sqrt{-1}$ is the imaginary unit and *C* is the measured capacitance. In this case, the electrical reactance $X_{\rm C}$ is defined as $X_{\rm C} = -1/(\omega C)$ and the phase angle θ_Z between the current and voltage can be calculated using

$$\theta_Z = \arctan\left(\frac{X_{\rm C}}{R_{\rm s}}\right) \tag{7}$$

The Supplementary Information document provides θ_z adherence curves for the poly-TiN/SiO₂/ITO/Al MISM at 10 kHz, 100 kHz, and 1 MHz. By performing a smallsignal analysis for the MISM capacitor structure, we calculated a negative bias resistance of 86.7 $\mu\Omega$ with a capacitance value of 29 fF/ μ m² at 20 GHz. These values, alongside the radius of the capacitor, yield an anticipated *RC* bandwidth of roughly 200 GHz, as obtained from calculated impedance parameters. It is worth noting that the large capacitor area relative to the thickness of the insulator and semiconductor layers yielded relatively small and large lumped series resistance and capacitance, respectively.

For an ITO layer with a $n_{\rm ITO} = 6.05 \times 10^{20} \text{ cm}^{-3}$ at 0.50 V and a small-signal frequency of 1 MHz, the calculated capacitance value based on simulations ranged between 1.9 and 3.07 fF/µm² depending on the ITO and SiO₂ layer thicknesses. The measured capacitance value at 0.50 V and 1 MHz small-signal frequency is 2.19 fF/µm² as can be seen in Fig. 7. This is within the calculated capacitance

range for an MISM device with around a 2.5 nm average increase in ITO and SiO_2 layer thicknesses. Therefore, we must note that variations in the actual structural layer thicknesses are not the only factor that affects the measured device parameters. Fabrication process imperfections and defects must have induced parasitic effects, which led to an increase in the "effective" dielectric and semiconductor layers thicknesses (i.e., the approximately 2.5 nm increase in ITO and SiO₂ layers), further contributing to lower measured capacitance levels.

As observed in Fig. 7, with a modest variation in negative bias levels, a significant drop in normalized capacitance levels occurred at higher positive bias levels, illustrating that higher current injection levels are achieved. This is a direct result of carrier accumulation at the SiO₂/ITO interface. This mechanism behind the dispersion properties of charge carriers within the semiconductive ITO layer induces the necessary capacitance modulation upon which optical modulation is directly dependent. At all small-signal frequency levels (refer to the Supplementary Information document), capacitance levels are the highest across MISM devices with F_{O_2} of 0.70 sccm (sample 3, $n_{\rm ITO} = 8.35 \times 10^{20}$ cm⁻³) and 0.80 sccm (sample 4, $n_{\rm ITO} = 6.05 \times 10^{20}$ cm⁻³), demonstrating relatively more robust capacitors when the device is operating close to or well within the ENZ regime. When comparing the CVmeasurements performed with a small-signal frequency component of 1 MHz (Fig. 7) with those with small-signal frequency components of 10 kHz and 100 kHz (refer to the Supplementary Information document), it is worth noting that the fabricated MISM devices display relatively highperformance levels when biased with small-signal frequency levels of 100 kHz and 1 MHz. At these smallsignal frequency levels, lower noise levels (at 100 kHz and 1 MHz small-signal frequencies) and higher areal capacitance levels (at 1 MHz small-signal frequency) were achieved while maintaining considerable modulation in capacitance values.

MISM devices with ITO films deposited at $F_{O_2} = 0.70$ and sccm have higher oxygen contents and therefore are less conductive. The ITO optical attributes described in Figure S1 of the Supplementary Information document illustrate how the dielectric constant, and hence the refractive index, varies with carrier concentration. As the carrier concentration increased through doping, there were points where the properties of ITO transitioned from those of a conductor to a semiconductor and then to an insulator⁶⁶. Therefore, the *CV* measurements done on these ITO films deposited at different F_{O_2} levels are expected to reflect a trend of increasing refractive index for higher $F_{O_2}^{67}$.

In Fig. 7, we can observe that at a negative bias around -1 V, there are dips in capacitance levels, where depletion occurs and $Re\{n\}$ drops, and hence the ITO electrical properties at the interface shift towards those of a conductive dielectric and thus start to exhibit smaller capacitance values. For small positive bias values (partial forward bias), we conjecture that the observed CV curves follow the $\operatorname{Re}\{n\}$ -V curve exhibited in Fig. 2b. As the bias increases, accumulation effects occur, contributing to higher capacitance levels. At negative bias levels, the shape of the CV curves resembles an inversion-region operation, and hence the capacitance levels start to increase again. We also observe what resembles a roll-out at higher positive bias levels, which is possible cause by other competing effects. For instance, enhanced optical confinement is possible, implying an enhanced overlap with the electric field, which lowers capacitance levels. This phenomenon can be explained by the effects of plasma and the correlations between optical parameters and carrier density⁶⁸. Re{ ε } is related to the energy stored within a medium and is affected by capacitance and $Im\{\varepsilon\}$ is associated with the loss or gain of energy within a medium. Capacitors with ITO films deposited at higher F_{0} , are more resistive and therefore exhibit higher $\operatorname{Re}\{\varepsilon\}$, which intuitively explains the greater capacitance levels displayed by ITO films deposited with $F_{O_2} = 0.70$ and 0.80 sccm. Finally, we note that as the operating frequency of the MISM devices gets higher, the CV curve gets smoother. This is probably caused by the noises being relatively lower in the driving frequency source. While for the 10 kHz operating frequency case, there are more noticeable slight dips in the capacitance levels around -1 V compared to higher operation frequencies. This may be caused by the higher modulation speed of carriers at the SiO2/ITO interface.

CHPW electrical characterization

Fig. 8a displays the forward-biased *IV* response of the CHPW, manifesting an irreversible oxide breakdown around 35 V. This corresponds to a SiO₂ dielectric strength of 17.5 MV/cm. The tunneling current up until 25 V bias was less than 2 nA, which indicates excellent capacitive coupling characteristics, and thus the shunt path bypassing the capacitor can be neglected (i.e., $R_{\text{MIS}} \rightarrow \infty$). Moreover, the device's capacitance was determined at an AC frequency and voltage of 1 MHz and 10 mV_{rms}, respectively. Because of the compact device footprint nature and instrument resolution limitation, the high-frequency branch of the MIS *CV* curve could not be observed. C_{MIS} for the 5- and 10-µm long devices were measured to be about 3 fF and 5 fF, respectively, at a bias

of 25 V. Fig. 8b displays the photocurrent characteristics. At 10 V, the MIS photodiode exhibited a photocurrent-to-dark ratio of 5.77.

Several contact resistance terms are considered when describing the modulator's electrical characteristics. The probe contact resistance is negligible as the coaxial highfrequency infinity waveguide probe used for device characterization has a typical contact resistance below 0.1 Ω to Al pads. The series resistance from the sputtered Al contact (around 5 Ω) is small relative to that of the other sputtered thin films, as their resistivities were measured to be between $8 \times 10^{-7} \Omega \cdot \text{cm}$ and $2.9 \times 10^{-4} \Omega \cdot \text{cm}$. Therefore, the modulator resistance is dominated by the series resistance R_s of ITO and the contact resistance R_c between Al and ITO. Based on the dimensions of the fingers and modulators, R_s was determined to be 911.2 Ω and 896.6 Ω for modulator lengths of 5 and 10 µm, respectively.

The R_c for the CHPW modulator was determined via circular transmission line measurement (CTLM). CTLM is preferred over standard transmission line measurement for devices with micron-scale areas as current crowding can be avoided, and electrical isolation is automatically

established⁶⁹. As shown in the inset in Fig. 9, the CTLM test structure consisted of a conducting circular inner region of radius *L*, an air gap of width *d*, and a conducting outer part^{70,71}. Specifically, the total resistance $R_{\rm T}$ between the internal and external contacts can be expressed as

$$R_{\rm T} = \frac{R_{\rm sh}}{2\pi L} (d + 2L_{\rm T})\mathbb{C},\tag{8}$$

where $R_{\rm sh}$ is the sheet resistance, \mathbb{C} is a correction factor, and $L_{\rm T}$ is the transfer length describing the average distance traveled by carriers within the semiconductor region. These two parameters were calculated as $\mathbb{C} = L/d \ln(1 + d/L)$ and $L_{\rm T} = \sqrt{\rho_{\rm c}/R_{\rm sh}}$, where $\rho_{\rm c} = R_{\rm c}(\pi L_{\rm T}^2)$ is the specific contact resistivity that takes into account all interfacial effects and effects from regions close to the interface⁷¹. CTLM results from the ITO/Al interface are depicted in Fig. 9. The conducting regions consisted of 250-nm-thick Al on 10-nm-thick ITO on SOI. Because ITO is a highly degenerate semiconductor, the barrier height and the width of the depletion region at the ITO/metal interface are small. Therefore, ITO forms an ohmic contact with metals, allowing for smooth carrier injection. Using the measured $R_{\rm sh}$ of 290 Ω/\Box , the $\rho_{\rm c}$ of the CTLM structures is extracted to be $7.2 \times 10^{-3} \Omega \cdot \text{cm}^2$. This is significantly lower than the $3 \times 10^{-1} \Omega \cdot cm^2$ previously reported for ITO/Al contacts with similar $R_{\rm sh}$ values⁷², but higher than $10^{-6}\Omega \cdot \text{cm}^2$ as estimated by the standard metal/semiconductor contact theory ⁷³. Such deviation from theoretical value is common for ITO devices, as the interaction between oxygen and metal has been observed to alter ITO's carrier density at the interface and thus leads to an increase in ρ_c . With contact area of 82.72 μ m², the R_c for the fabricated CHPW modulators was measured to be 8.7 kΩ.

Fig. 9 Contact resistance characterization — **a** A plot summarizing CTLM results for the Al (250 nm)/ITO (10 nm) contacts with L = 75 µm. **b** *IV* curves for a CTLM structure with d = 10 µm and L = 75 µm.





CHPW optical modulator characterization

Lower carrier concentrations lead to lower optical losses, which result in better modulator's IL but at the expense of lower conductivity, implying lower *RC* time constants. Therefore, we require the carrier mobility to be as high as possible to increase the conductivity without increasing the carrier concentration, leading to lower insertion and optical losses. The sheet resistivity of ITO is strongly correlated with the O_2 and Sn contents. The density of free electrons in ITO is directly influenced by O_2 vacancies, with an inverse proportionality to the O_2 content. On the other hand, the electron mobility in ITO is heavily influenced by the O_2 content, as higher O_2 contents enhance the crystallization of ITO thin films⁷⁴.

CHPW unbiased response

Unbiased-state CHPW modulator characterization has been performed using the cut-back method. As observed in Fig. 10, the IL and CE at $\lambda = 1550$ nm were extracted to be around 0.128 dB/µm and 52.50%, respectively. The loss value is higher than the simulated value of 0.03 dB/µm (simulations are not shown here). The higher experimental IL level is attributed to the additional free carrier absorption caused by elevated ITO carrier density and scattering losses from the contact region. Effects from deposited layer roughnesses and various intrinsic defects, such as surface states and oxygen vacancies, could have played an additional role in this higher measured IL level^{75–77}. Nonetheless, IL and CE values exhibit low variations between $\lambda = 1520$ nm and 1600 nm, indicating a potential broadband modulator operation.

CHPW DC response

Fig. 11a plots the transmission of 10-µm-long CHPW modulators under forward bias. The maximum voltage was kept below 26 V to avoid oxide breakdown, and the results have been normalized to optical transmission at zero bias.



We note that the observed optical transmission level decreases marginally to a small extent as the voltage is increased up to 20 V. After the applied voltage exceeds 20 V, a dramatic increase in optical absorption takes place, and transmission is reduced to -10 dB at 25 V, which corresponds to strong ER of approximately 1 dB/µm, one of the highest measured to-date to our knowledge⁶. The reason for resorting to applying a high voltage level of 20 V is that a 20-nm-thick SiO_2 (rather than a high- κ dielectric material) layer was incorporated in the MOS region of the modulator for simplicity of design, hence the facile integration of SiO₂/ITO. In other words, our CHPW design necessitates applying a relatively high electric field, given the relatively low dielectric constant of SiO₂, which serves as a reference to other field-confining materials. The voltage can be reduced to improve the modulation efficiency by incorporating a high-k dielectric material instead, such as hafnium oxide (HfO₂).

The behavior of the same modulator without an ITO layer is also provided for comparison. As no modulation can be observed under both scenarios, the measured modulation response can be attributed to field-induced carrier accumulation rather than drift in the set-up, optothermal effects at high bias voltages, or optoelectronic events in materials other than ITO. Moreover, modulation depth varies with device length, and the normalized transmission for a 15-µm-long modulator can reach -12 dB at 26 V as can be seen in Fig. 11c, where the broadband response of the CHPW modulator is shown. It was verified by measuring the optical transmission as a function of voltage at different wavelengths (from $\lambda = 1.53 - 1.6 \ \mu m$), as shown in the figure. Beyond $\lambda = 1550$ nm, the modulation depth starts to decrease as the permittivity of ITO moves away from the ENZ regime. However, an ER of about 1 dB/µm was maintained between $\lambda = 1.53$ µm and 1.56 µm.

CHPW AC response

Fig. 11d depicts the 10-µm-long modulator's frequency response. One can observe that the frequency response is flat up to about 26 GHz, and the calculated 3-dB cutoff frequency (i.e., anticipated *RC* bandwidth), given a parasitic capacitance of 5 fF, is approximately 636 GHz for 50 Ω load resistance. The frequency response measurement, including the substrate characteristics and effects from the RF probe, was normalized to the response peak point. Using small-signal analysis, we calculated the junction current at 0 V. We extracted the resistance from the real part of the resulting impedance for operating frequencies up to 636 GHz at the CHPW's SiO₂/ITO heterojunction. At static and up to 26 GHz, the resistance was found to be around 75.6 Ω at 0 V, while the junction



CHPW modulators as functions of bias voltage. **c** Normalized transmission curves of a $10-\mu$ m-long SiO₂/ITO-based CHPW modulator as functions of bias voltage and wavelength. **d** Optoelectronic bandwidth measurements of the SiO₂/ITO-based CHPW modulator.

capacitance was calculated numerically using the finite difference method (i.e., dv/dq with infinitesimal voltage steps) and was estimated to be around 0.21 fF/µm (normalized to the propagation distance). For operating frequencies from 26 to above 636 GHz (up to 700 GHz), the heterojunction resistance and capacitance levels dropped dismally to approximately 73.6 Ω and 0.18 fF/µm, respectively.

The modulation speed of a CHPW is determined by two factors: (1) the time the accumulation layer inside the semiconductor takes to form, and (2) the delay time arising from parasitic *RC* effects. Electron accumulation is a relatively fast process dictated by majority carrier dynamics. The formation time can be estimated using $\tau = t/v_{drift}$, where, in our case, $t = t_{TTO} = 10$ nm and v_{drift} are the ITO film thickness and the drift velocity of carriers in ITO, respectively. Here, v_{drift} can be estimated using $v_{drift} = \mu E$, where μ is the carrier mobility in ITO and *E* is the applied electric field. The latter is proportional to the magnitude of applied gate voltage divided by the dielectric film thickness ($t_{SiO_2} = 20$ nm). Using $\mu = 33$ cm²/(V·s) as obtained from Hall measurements, the resulting modulation speed exceeds 300 THz. Similarly, the electron scattering rate of ITO is around 28.65 THz as derived from the collision frequency ($\gamma = 1.8 \times 10^{14}$ rad/s); hence, the modulator speed is also not limited by the transient response of the accumulation layer when the gate is turned off⁷⁸. Thus, similar to other MIS-based modulators, our CHPW modulator's speed is dictated by the RC time constant⁷⁹. While the *RC* response of the 10- μ m-long CHPW modulator has an anticipated 3-dB cutoff frequency above 600 GHz, the bandwidth of the testing instrument used to characterize the modulator is limited to 26 GHz. Because the response of light to the plasma dispersion effect is significantly faster than the RC limit, delays from strong local field decays can be disregarded, and, as a result, the theoretical electrical modulation speed of 636 GHz is directly relevant to the optical domain.

CHPW ER analysis

The performance of the 10-µm-long CHPW modulator was characterized over broad wavelength and temperature ranges. The evolution in the modulator's ER level at elevated stage temperatures (T = 35-100 °C) relative to the modulator's response at room temperature (ΔER_{RT} ,



calculated as an absolute numerical difference) is shown Fig. 12 as a function of voltage. Because of power output limitations in the thermoelectric cooler (TEC) source meter, the Peltier heat pump requires a voltage-limited mode of operation, and, therefore, the stage temperature exhibited a ±0.2 °C fluctuation. Regardless of the noise caused by temperature fluctuations, the modulator's ER performance did not degrade; instead, it increased with temperature. increasing stage For instance. an approximately 0.74 dB increase in ER was detected at 50 °C and 100 °C at 25 V.

Concluding remarks

We have successfully demonstrated the facile growth, integration, and characterization of Al/ITO/SiO₂ MISM heterojunctions on a poly-TiN/Si platform, facilitating the design and fabrication of practical CHPW devices. The research focus on oxide materials for plasmon-electronics has significantly surged, given its potential to achieve tunable material characteristics. However, achieving optimal device performance requires extended optimization of material quality, device design, and process technology. Herein, we focused on developing insulator–semiconductor device topologies by integrating an electro-optic SiO₂/ITO

interface in MIS devices housed on bulk Si and SOI platforms. The advantage of this integration scheme is rooted in the use of CMOS-compatible materials, along with breaking the loss-confinement barrier in plasmonelectronic devices by tuning the waveguide architectural characteristics and hence achieving control over supermode attributes. XRD, IV, CV, and parameter analyzer measurements were used to characterize the grown materials and fabricated devices. The fabricated CHPW modulator shows ER and IL levels of around 1 dB/µm and 0.128 dB/µm, respectively, for a 10-µm-long waveguide length. While our initial device performance seems promising, challenges still exist, and these are the development of the ability to produce large-area optoelectronic devices using current material synthesis and device fabrication methodologies. Table 2 summarizes our CHPW modulator performance and provides performance comparison with select modulator configurations as reported in the literature.

Materials and methods

Thin film deposition and material characterization

The ITO and a-Si thin films were deposited using an AJA International twin chamber RF magnetron sputtering system (ATC Orion Series). The ITO and a-Si deposition processes were performed at room temperature with a working pressure of 3 mTorr. The magnetron power was fixed at 150 W and 300 W for the ITO and a-Si targets, respectively. During the a-Si thin film sputtering, an Ar gas flow of 30 sccm was flown for 200 seconds, yielding a 200-nm-thick thin film.

The ITO target was 3 inches in diameter which is 90% In₂O₃ by weight. Multiple ITO thin films were deposited with an Ar gas flow rate set at 50 sccm at room temperature. The O₂ flow rate was varied as follows: $F_{O_2} = 0.50$ (sample 1, $n_{\text{ITO}} = 2.28 \times 10^{21} \text{ cm}^{-3}$), $F_{O_2} = 0.60 \text{ sccm}$ (sample 2, $n_{\text{ITO}} = 1.74 \times 10^{21} \text{ cm}^{-3}$), $F_{O_2} = 0.70 \text{ sccm}$ (sample 3, $n_{\text{ITO}} = 8.35 \times 10^{20} \text{ cm}^{-3}$), and $F_{O_2} = 0.80 \text{ sccm}$ (sample 4, $n_{\text{ITO}} = 6.05 \times 10^{20} \text{ cm}^{-3}$). This was done to

 Table 2
 Summary of fabricated CHPW modulator performance parameters, along with performance comparison with select modulator configurations.

Modulator device structure	Footprint (µm²)	Speed (GHz)	Operation wavelength (nm)	Driving voltage (V)	ER (dB)	Ref.
MIS–Schottky CHPW	10 × 0.2	>600	1550	25	10.63	This work
MISM capacitor	3×10^4	>200	1550	15	-	This work
Plasmonic Si Mach–Zehnder	10 × 1	>70	1550	3	6	Haffner et al. ⁸⁰
Graphene-based Si waveguide	50 × 10	5.9	1550	2.5	5.2	Hu et al. ⁸¹
Electro-optic graphene	1.5 × 30	>150	1570	10	28	Phare et al. 82

demonstrate the effects of varying the gas flow on the conductivity of the deposited films. To optimize the material deposition process for optimal conductivity, ITO thin films were deposited on fused silica substrates, then characterized electrically using Hall effect measurements to determine the carrier concentration n and optically using ellipsometry to determine their thicknesses. The growth conditions of sample 4 were ultimately chosen to deposit the ITO thin films used in the MISM and CHPW device fabrication processes, given that it resulted in an optimal modulator's IL (detailed optimization results are not shown here for conciseness).

X-ray diffraction crystallography

Crystal structure properties of the deposited TiN thin film were examined by a Panalytical MRD glancing incidence XRD (GIXRD) system using copper (Cu) $K\alpha$ radiation in line mode. On the incident side, the system is equipped with a mirror and slits, whereas on the receiving side, the system is equipped with a parallel plate collimator.

Electronic properties

The electrical properties of TiN and ITO, namely the charge carrier density and mobility, as well as the electrical resistivity and Hall coefficient ($R_{\rm H}$), were determined at room temperature in a van der Pauw configuration of electrodes using a Nanometrics HL5500 Hall measurement system with a constant magnetic flux density of 0.504 T.

MISM: The MISM *CV-IV* measurements were performed in an electrical probe station equipped with an Everbeing International Corp. probe station C-8 with a shielding box and vibration isolation. The measurements were collected and analyzed using a Keithley 4200A-SCS Parameter Analyzer with a supply voltage range of 100–240 V_{rms} at 50 or 60 Hz and 1000 VA current rating.

CHPW: The *IV* response of a 10-µm-long Al/SiO₂/ITO CHPW structure was measured using an HP 4155A semiconductor parameter analyzer. The device capacitance was determined using an HP 4280 *CV* meter. Moreover, the optoelectronic bandwidth of the CHPW modulators up to 6 GHz was measured using an RF signal that was generated by a National Instrument (NI) PXIe-5673E RF vector signal generator (VSG) with 6 dBm peak-to-peak amplitude and a rectangular shape. A bias-tee set before the input of the RF probe was used to combine the RF signal with DC offset from a Keithley 2604B source meter. The resulting amplitude-modulated optical signal was captured via a New Focus 1454 18.5 ps Vis-IR photodetector and amplified with an AMF 00101000-55 amplifier before being fed into an NI PXIe-5663E vector signal analyzer (VSA) for analysis. The electrical bandwidth of the CHPW photodetector was quantified using the NI PXIe-5673E VSG and PXIe-5663E VSA. On the input side, the VSG stimulus was amplified and drove a Fujitsu LiNbO₃ Mach–Zehnder modulator, generating intensity-modulated optical signals up to 6 GHz. On the output side, the photocurrent was collected with a coaxial high-frequency Infinity waveguide probe and amplified before feeding into the NI PXIe-5663E VSA. Measurements with the laser beam turned off were also performed to subtract coherent electrical input-output crosstalk. For measurement between 6 and 26 GHz, the same setup with Keysight M9375A PXIe vector network analyzer (26.5 GHz, 6-port) and AMF-4F060180 amplifier were used.

Atomic force microscopy

The surface morphology of deposited crystals was assessed using Bruker Dimension FastScan atomic force microscope operating in tapping mode. The images were recorded from 4 μ m × 4 μ m areas with a resolution of 1024 × 1024 pixels at a scan rate of 1 Hz, using a commercial ScanAsyst-Air pyramidal silicon nitride probe.

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Author contributions

Alfaraj, Lin, and Helmy proposed the ideas and initiated the project. Alfaraj, Nasif, and Rajput performed the theoretical analysis. Alfaraj, Lin, and Nasif collected and analyzed the experimental data. Alfaraj wrote the manuscript. Helmy supervised the study.

Conflict of interest

The authors declare that they have no conflicts of interest.

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References

- Jiang, W. Y. et al. Free-standing nanoarrays with energetic electrons and active sites for efficient plasmon-driven ammonia synthesis. *Small* 18, 2201269 (2022).
- 2. Schörner, C. & Lippitz, M. Single molecule nonlinearity in a plasmonic

waveguide. Nano Letters 20, 2152-2156 (2020).

- Gadalla, M. N. et al. Imaging of surface plasmon polaritons in low-loss highly metallic titanium nitride thin films in visible and infrared regimes. *Optics Express* 28, 14536-14546 (2020).
- Gramotnev, D. K. & Bozhevolnyi, S. I. Plasmonics beyond the diffraction limit. *Nature Photonics* 4, 83-91 (2010).
- Colom, R. et al. Enhanced Purcell factor for nanoantennas supporting interfering resonances. *Physical Review Research* 4, 023189 (2022).
- Lin, C. C. et al. Monolithic plasmonic waveguide architecture for passive and active optical circuits. *Nano Letters* 20, 2950-2957 (2020).
- Su, Y. et al. Record Purcell factors in ultracompact hybrid plasmonic ring resonators. *Science Advances* 5, eaav1790 (2019).
- Purcell, E. M. Spontaneous emission probabilities at radio frequencies. in Confined Electrons and Photons: New Physics and Applications (eds Burstein, E. & Weisbuch, C.) (Boston: Springer, 1995), 839-839.
- Lafone, L., Sidiropoulos, T. P. H. & Oulton, R. F. Silicon-based metalloaded plasmonic waveguides for low-loss nanofocusing. *Optics Letters* 39, 4356-4359 (2014).
- Wang, F. W. et al. CMOS-compatible electronic-plasmonic transducers based on plasmonic tunnel junctions and Schottky diodes. *Small* 18, 2105684 (2022).
- Alfaraj, N. et al. Deep-ultraviolet integrated photonic and optoelectronic devices: a prospect of the hybridization of group III–nitrides, III–oxides, and two-dimensional materials. *Journal of Semiconductors* **40**, 121801 (2019).
- Xu, K. K. Integrated silicon directly modulated light source using p-well in standard CMOS technology. *IEEE Sensors Journal* 16, 6184-6191 (2016).
- Hoffmann, M. et al. Conjugated polymer–gold–silver hybrid nanoparticles for plasmonic energy focusing. *The Journal of Physical Chemistry C* 126, 2475-2481 (2022).
- Naik, G. V., Shalaev, V. M. & Boltasseva, A. Alternative plasmonic materials: beyond gold and silver. *Advanced Materials* 25, 3264-3294 (2013).
- Amin, R. et al. Heterogeneously integrated ITO plasmonic Mach–Zehnder interferometric modulator on SOI. Scientific Reports 11, 1287 (2021).
- Kwon, M. S. Discussion of two ways of optically modeling indium–tin–oxide layers in slot waveguides for waveguide analysis. *IEEE Photonics Journal* 8, 4900108 (2016).
- Baek, J., You, J. B. & Yu, K. Free-carrier electro-refraction modulation based on a silicon slot waveguide with ITO. *Optics Express* 23, 15863-15876 (2015).
- Lee, H. W. et al. Nanoscale conducting oxide PlasMOStor. Nano Letters 14, 6463-6468 (2014).
- Kim, J. T. Silicon optical modulators based on tunable plasmonic directional couplers. *IEEE Journal of Selected Topics in Quantum Electronics* 21, 3300108 (2015).
- Zhao, H. W. et al. Broadband electroabsorption modulators design based on epsilon-near-zero indium tin oxide. *IEEE Journal of Selected Topics in Quantum Electronics* **21**, 192-198 (2015).
- Zhu, S. Y., Lo, G. Q. & Kwong, D. L. Design of an ultra -compact electroabsorption modulator comprised of a deposited TiN/HfO₂/ITO/Cu stack for CMOS backend integration. *Optics Express* 22, 17930-17947 (2014).
- Vasudev, A. P. et al. Electro-optical modulation of a silicon waveguide with an "epsilon-near-zero" material. *Optics Express* 21, 26387-26397 (2013).
- Melikyan, A. et al. Surface Plasmon polariton absorption modulator. Optics Express 19, 8855-8869 (2011).
- Feigenbaum, E., Diest, K. & Atwater, H. A. Unity order index change in transparent conducting oxides at visible frequencies. *Nano Letters* 10,

2111-2116 (2010).

- 25. Liberal, I. et al. Photonic doping of epsilon-near-zero media. *Science* **355**, 1058-1062 (2017).
- 26. Engheta, N. Pursuing near-zero response. Science 340, 286-287 (2013).
- Wu, C. et al. Quantum hybrid plasmonic nanocircuits for versatile polarized photon generation. *Advanced Optical Materials* **10**, 2101596 (2022).
- Bolognesi, M. et al. A fully integrated miniaturized optical biosensor for fast and multiplexing plasmonic detection of high-and low-molecularweight analytes. *Advanced Materials* 35, 2208719 (2023).
- 29. Haffner, C. et al. Low-loss Plasmon-assisted electro-optic modulator. *Nature* **556**, 483-486 (2018).
- Khurgin, J. B. How to deal with the loss in plasmonics and metamaterials. *Nature Nanotechnology* 10, 2-6 (2015).
- Wassel, H. M. G. et al. Opportunities and challenges of using plasmonic components in nanophotonic architectures. *IEEE Journal on Emerging* and Selected Topics in Circuits and Systems 2, 154-168 (2012).
- Lu, Z. L., Zhao, W. S. & Shi, K. F. Ultracompact electroabsorption modulators based on tunable epsilon-near-zero-slot waveguides. *IEEE Photonics Journal* 4, 735-740 (2012).
- Chang, K. H. et al. Enhancing on/off ratio of a dielectric-loaded plasmonic logic gate with an amplitude modulator. *Scientific Reports* 13, 5020 (2023).
- Maier, M. et al. Ultracompact amplitude modulator by coupling hyperbolic polaritons over a graphene-covered gap. ACS Photonics 5, 544-551 (2018).
- Alfaraj, N. et al. Silicon-integrated monocrystalline oxide-nitride heterostructures for deep-ultraviolet optoelectronics. *Optical Materials Express* 11, 4130-4144 (2021).
- Alfaraj, N. et al. Heteroepitaxial β-Ga₂O₃ on conductive ceramic templates: toward ultrahigh gain deep-ultraviolet photodetection. *Advanced Materials Technologies* 6, 2100142 (2021).
- Gadalla, M. N. et al. Excitation of strong localized surface Plasmon resonances in highly metallic titanium nitride nano-antennas for stable performance at elevated temperatures. ACS Applied Nano Materials 2, 3444-3452 (2019).
- Feng, X. et al. Photonic approach for generation and fast switching of binary digitally modulated RF signals. *IEEE Photonics Journal* 12, 5502208 (2020).
- Liu, X. G. et al. Electrical tuning of a quantum plasmonic resonance. Nature Nanotechnology 12, 866-870 (2017).
- Liu, X. G. et al. Quantification and impact of nonparabolicity of the conduction band of indium tin oxide on its plasmonic properties. *Applied Physics Letters* **105**, 181117 (2014).
- 41. Boltasseva, A. & Atwater, H. A. Low-loss plasmonic metamaterials. Science **331**, 290-291 (2011).
- 42. Franzen, S. et al. Plasmonic phenomena in indium tin oxide and ITO-Au hybrid films. *Optics Letters* **34**, 2867-2869 (2009).
- Losego, M. D. et al. Conductive oxide thin films: model systems for understanding and controlling surface Plasmon resonance. *Journal of Applied Physics* **106**, 024903 (2009).
- Azani, M. R., Hassanpour, A. & Torres, T. Benefits, problems, and solutions of silver nanowire transparent conductive electrodes in indium tin oxide (ITO)-free flexible solar cells. *Advanced Energy Materials* 10, 2002536 (2020).
- 45. Chen, Z. X. et al. Fabrication of highly transparent and conductive indium–tin oxide thin films with a high figure of merit via solution processing. *Langmuir* **29**, 13836-13842 (2013).
- 46. Rodrigo, D. et al. Mid-infrared plasmonic biosensing with graphene. *Science* **349**, 165-168 (2015).
- 47. Gleiter, H. et al. Nanocrystalline materials: a way to solids with tunable electronic structures and properties?. *Acta Materialia* **49**, 737-745

(2001).

- Sagmeister, M. et al. Electrically tunable resistance of a metal. *Physical Review Letters* 96, 156601 (2006).
- Park, J. et al. Electrically tunable epsilon-near-zero (ENZ) metafilm absorbers. *Scientific Reports* 5, 15754 (2015).
- Berini, P. Plasmon-polariton waves guided by thin lossy metal films of finite width: bound modes of symmetric structures. *Physical Review B* 61, 10484-10503 (2000).
- Oulton, R. F. et al. A hybrid plasmonic waveguide for subwavelength confinement and long-range propagation. *Nature Photonics* 2, 496-500 (2008).
- Alfaraj, N. et al. Optical and interfacial characteristics of a heterojunction between (01)-oriented single domain β-(In_{0.072}Ga_{0.928})₂O₃ and α-Al₂O₃ crystals. Optical Materials Express 12, 3273-3283 (2022).
- Worfolk, B. J. et al. Ultrahigh electrical conductivity in solution-sheared polymeric transparent films. *Proceedings of the National Academy of Sciences of the United States of America* **112**, 14138-14143 (2015).
- Itoh, S. & Maruyama, K. Recoveries of metallic indium and tin from ITO by means of pyrometallurgy. *High Temperature Materials and Processes* 30, 317-322 (2011).
- Minami, T. Transparent conducting oxide semiconductors for transparent electrodes. *Semiconductor Science and Technology* 20, S35-S44 (2005).
- Yu, H. K. et al. Nano-branched transparent conducting oxides: beyond the brittleness limit for flexible electrode applications. *Nanoscale* 4, 6831-6834 (2012).
- 57. Reineke, S. et al. White organic light-emitting diodes with fluorescent tube efficiency. *Nature* **459**, 234-238 (2009).
- Sun, Y. R. & Forrest, S. R. Enhanced light out-coupling of organic lightemitting devices using embedded low-index grids. *Nature Photonics* 2, 483-487 (2008).
- Park, S. et al. Self-powered ultra-flexible electronics via nano-gratingpatterned organic photovoltaics. *Nature* 561, 516-521 (2018).
- Zhao, G. Q. et al. Optical transmittance enhancement of flexible copper film electrodes with a wetting layer for organic solar cells. ACS Applied Materials & Interfaces 9, 38695-38705 (2017).
- Alfaraj, N. et al. Functional integrity of flexible n-channel metal-oxide-semiconductor field-effect transistors on a reversibly bistable platform. *Applied Physics Letters* **107**, 174101 (2015).
- 62. Na, H. et al. Enhanced CO oxidation and cyclic activities in threedimensional platinum/indium tin oxide/carbon black electrocatalysts processed by cathodic arc deposition. ACS Applied Materials & Interfaces 11, 25179-25185 (2019).
- 63. Liu, Y. & Mustain, W. E. Stability limitations for $Pt/Sn-In_2O_3$ and $Pt/In-SnO_2$ in acidic electrochemical systems. *Electrochimica Acta* **115**, 116-125 (2014).
- Koch, U. et al. Digital plasmonic absorption modulator exploiting epsilon-near-zero in transparent conducting oxides. *IEEE Photonics Journal* 8, 4800813 (2016).
- Lin, C. C. C. Photonic devices using coupled plasmonic structures. PhD thesis, University of Toronto, Toronto, 2019.
- Jiang, W. F., Miao, J. Y. & Li, T. Silicon mode-selective switch via horizontal metal-oxide-semiconductor capacitor incorporated with ENZ-ITO. *Scientific Reports* **9**, 17777 (2019).
- 67. Tien, C. L. et al. Effect of oxygen flow rate on the optical, electrical, and mechanical properties of DC sputtering ITO thin films. *Advances in Condensed Matter Physics* **2018**, 2647282 (2018).
- Soref, R. A. & Bennett, B. R. Kramers-Kronig analysis of electro-optical switching in silicon. Proceedings of SPIE 0704, Integrated Optical Circuit Engineering IV. Cambridge, MA, United States: SPIE, 1987, 32-37.

- 69. Cohen, S. S. & Gildenblat, G. S. Metal-Semiconductor Contacts and Devices. (London: Academic, 1986).
- Reeves, G. K. Specific contact resistance using a circular transmission line model. *Solid-State Electronics* 23, 487-490 (1980).
- Schroder, D. K. Semiconductor Material and Device Characterization. (Hoboken: John Wiley & Sons, 2006).
- Rastogi, A. C. & Lakshmikumar, S. T. Indium-tin-oxide-metal interfacial resistance and its implication for solar cells. *Solar Cells* 26, 323-328 (1989).
- Chang, C. Y., Fang, Y. K. & Sze, S. M. Specific contact resistance of metalsemiconductor barriers. *Solid-State Electronics* 14, 541-550 (1971).
- Buchanan, M., Webb, J. B. & Williams, D. F. Preparation of conducting and transparent thin films of tin-doped indium oxide by magnetron sputtering. *Applied Physics Letters* 37, 213-215 (1980).
- Wu, Z. X. et al. Micro metal additive manufactured low-loss slotted rectangular waveguides operating at 220- 500 GHz. *Frontiers in Physics* 9, 696318 (2021).
- 76. Fiorese, V. *et al.* Evaluation of micro laser sintering metal 3D-printing technology for the development of waveguide passive devices up to 325 GHz. Proceedings of the 2020 IEEE/MTT-S International Microwave Symposium (IMS). Los Angeles, CA, USA: IEEE, 2020, 1168-1171.
- AlAloul, M. & Rasras, M. Low insertion loss plasmon-enhanced graphene all-optical modulator. ACS Omega 6, 7576-7584 (2021).
- Michelotti, F. et al. Thickness dependence of surface plasmon polariton dispersion in transparent conducting oxide films at 1.55 μm. Optics Letters 34, 839-841 (2009).
- Liu, A. S. et al. A high-speed silicon optical modulator based on a metal–oxide–semiconductor capacitor. *Nature* 427, 615-618 (2004).
- Haffner, C. et al. All-plasmonic Mach-Zehnder modulator enabling optical high-speed communication at the microscale. *Nature Photonics* 9, 525-528 (2015).
- Hu, Y. T. et al. Broadband 10 Gb/s operation of graphene electroabsorption modulator on silicon. *Laser & Photonics Reviews* 10, 307-316 (2016).
- Phare, C. T. et al. Graphene electro-optic modulator with 30 GHz bandwidth. *Nature Photonics* 9, 511-514 (2015).
- Zhang, B. & Zirath, H. Metallic 3-D printed rectangular waveguides for millimeter-wave applications. *IEEE Transactions on Components*, *Packaging and Manufacturing Technology* 6, 796-804 (2016).
- Alfaraj, N. *et al.* Heteroepitaxial growth method of compound semiconductor materials on multi-oriented semiconductor substrates and devices (2021).
- Gong, C. & Leite, M. S. Noble metal alloys for plasmonics. ACS Photonics 3, 507-513 (2016).
- Emmott, C. J. M., Urbina, A. & Nelson, J. Environmental and economic assessment of ITO-free electrodes for organic solar cells. *Solar Energy Materials and Solar Cells* 97, 14-21 (2012).
- Itoh, S., Osamura, H. & Komada, K. Thermodynamics of indium-tinoxygen ternary system. *Materials Transactions* 52, 1192-1199 (2011).
- Yang, C. W. & Park, J. W. The cohesive crack and buckle delamination resistances of indium tin oxide (ITO) films on polymeric substrates with ductile metal interlayers. *Surface and Coatings Technology* **204**, 2761-2766 (2010).
- Cairns, D. R. et al. Strain-dependent electrical resistance of tin-doped indium oxide on polymer substrates. *Applied Physics Letters* 76, 1425-1427 (2000).
- Hümmer, T. et al. Weak and strong coupling regimes in plasmonic QED. *Physical Review B* 87, 115419 (2013).
- Nicollian, E. H. & Brews, J. R. MOS (Metal Oxide Semiconductor) Physics and Technology. (New York: Wiley, 1982).
- Ma, Z. Z. et al. Compact graphene plasmonic slot photodetector on silicon-on-insulator with high responsivity. ACS Photonics 7, 932-940

(2020).