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Anisotropic optical and magnetic response in self-assembled TiN-$CoFe_2$ nanocomposites

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Abstract:

Transition metal nitrides (e.g., TiN) have shown tremendous promise in optical metamaterials for nanophotonic devices due to their plasmonic properties comparable to noble metals and superior high temperature stability. Vertically aligned nanocomposites (VANs) offer a great platform for combining two dissimilar functional materials with a one-step deposition technique toward multifunctionality integration and strong structural/property anisotropy. Here we report a two-phase nanocomposite design combining ferromagnetic $CoFe_2$ nanosheets in the plasmonic TiN matrix as a new hybrid plasmonic metamaterial. The hybrid metamaterials exhibit obvious anisotropic optical and magnetic responses, as well as a pronounced magneto-optical coupling response evidenced by MOKE measurement, owing to the novel vertically aligned structure. This work demonstrates a new TiN-based metamaterial with anisotropic properties and multi-functionality towards optical switchable spintronics, magnetic sensors and integrated optics.

Key Words: Vertically aligned nanocomposites; Tunable microstructure; Hyperbolic metamaterial; Magnetic anisotropy; Magneto-optical coupling

Introduction

Optical metamaterials consist of artificially designed nanostructured materials which generate unique optical properties that are not exhibited in natural materials. These novel optical properties, including negative refractive index[1,2], near-zero-index[3], and hyperbolic dispersion[4,5], originate from the confinement of light propagation in nanostructured materials. Noble metals (e.g., Au and Ag) are widely used in forming nanostructured plasmonic metamaterials due to their strong surface plasmon resonance. However, plasmonic metals exhibit high optical loss in the visible to near-infrared (vis-NIR) region due to inter-band and intra-band transitions[6]. In addition, other challenges in terms of fabrication and integration, as well as permittivity tuning of plasmonic metamaterials, greatly hinder their performances and applications[7]. Therefore, seeking alternative plasmonic materials is necessary to overcome these drawbacks. Transition metal nitrides (e.g. TiN, TaN, ZrN, etc) are promising candidates for plasmonic applications because of their metallic response in most optical wavelengths and high structural stability. Tailoring stoichiometry in nitrides allows tuning of optical properties easily[8]. Considering the fabrication and integration challenges of metals, transition metal nitrides are compatible with the complementary metal-oxide-semiconductor (CMOS) process and can be easily integrated on various substrates (e.g., MgO, STO, Si, sapphire)[9,10]. Besides, the high mechanical strength and high melting temperature enable them to be promising materials for future high temperature plasmonic applications[11,12].

With the development of nanofabrication techniques, various nanostructured nitrides have been demonstrated for plasmonic applications, e.g., periodic array of TiN nanoparticles[13], nanoantennas[14], nanotrenchs[15], and nanorings[16]. The integration of TiN with dielectric materials (e.g., AlN, MgO) into a multilayer structure has been explored exhibiting hyperbolic dispersion[17,18]. However, most of these TiN-based metamaterials rely on high-cost fabrication techniques, including e-beam lithography and focused ion-beam process. Compared to the conventional fabrication methods, a cost-effective self-assembly approach to growing hybrid materials into a vertically aligned nanocomposite (VANs) form has recently attracted tremendous interest. Multiple two-phase nitride-metal nanocomposites[19–21], such as TaN-Au, TiN-Au, and TiN-Ag, have been successfully demonstrated in VANs with enhanced surface plasmon resonance and nonlinear optical responses. Taking advantage of these simple self-assembly VAN platforms, other nitride-based nanostructures can be further derived by additional processes. For example, TiN nanohole arrays have been achieved by selectively etching away the Au nanopillars from TiN-Au VANs[22], and a 3D plasmonic framework is formed by alternating TiN-Au and TaN-Au layers[23]. Most of the prior demonstrations have been focusing on nitride-metal[19–21] or oxide-metal[24–29] systems as hybrid metamaterials.

Another opportunity brought by the designs of VANs is integrating different functionalities in one material system. Functional materials are a large material family with a wide selection of properties, such as plasmonic (e.g., Au[7]), superconductivity (e.g., $YBa_2Cu_3O_{7-\delta}$[30]), ferromagnetic (e.g., $CoFe_2O_4$[31], $MnFe_2O_4$[32], $CoFe_2$[33]), ferroelectricity (e.g., $BaTiO_3$[34]), and multiferroicity (e.g., $BiFeO_3$[35]) etc. Multifunctionality, as well as coupling effects, have been demonstrated in oxide-based VANs, such as magneto-electric coupling [36–38] and magneto-optic coupling effects [25,39,40]. On the other hand, most of the previous nitride-based VANs focus on incorporating plasmonic metal nanopillars towards optical tunability. Therefore, incorporating a secondary functional phase into the nitride matrix could enormously broaden the nitride VAN designs with other functionality. However, such nitride-based nanocomposite demonstration is very limited due to the challenges in material design incompatibility and differences in growth parameters required for the different phases.

In this work, we report a new hybrid metamaterial system of TiN-based nanocomposite with ferromagnetic $CoFe_2$ in the VAN form with strong anisotropic optical and magnetic properties. Here, ferromagnetic $CoFe_2$ nanopillars were formed by reducing $CoFe_2O_4$ in the target material during the high vacuum condition required by TiN growth. The TiN-$CoFe_2$ VANs are expected to exhibit optical and magnetic anisotropy as well as potential magneto-optical coupling. Laser frequency is varied to be 2 Hz and 10 Hz to effectively tune the dimension of $CoFe_2$ pillars. This demonstration shows the potential of designing new nitride-based VAN systems with multifunctionalities, property coupling, as well as effective property tunability.

Results and Discussion

The microstructure of TiN-$CoFe_2$ nanocomposites thin films was first characterized by XRD analysis using θ-2θ scans as shown in Fig. S1. An obvious out-of-plane of TiN (002), and MgO (002) can be clearly observed in the 2 Hz and 10 Hz deposited samples. The peak at the right side of the substrate MgO peak (2θ=43.254°) can be identified as $CoFe_2$ (011). The out-of-plane d-spacing of CoFe2 (011) was determined by 2.09 Å which is in 3.5% strain compared to its bulk value 2.02 Å. To reveal the detailed chemical distribution and 2-phase morphology in the system, a scanning transmission electron microscopy (STEM) analysis along with energy-dispersive X-ray spectroscopy (EDS) mapping was conducted on the samples in both cross-section and plan-view directions. As shown in the cross-sectional (Fig. 1b) and plan-view (Fig. 1d) STEM images, the two-phase nanocomposites exhibit a nanosheet-in-matrix structure. In the STEM images taken using the high angle annular dark field (HAADF) detector, the contrast is proportional to the atomic number (i.e., $\sim Z^{1.7}$) [41–43]. Therefore, the brighter nanosheet region is related to the higher atomic number of Co (Z = 26) and Fe (Z = 27), compared to TiN (averaged Z = 14.5). The EDS maps in Fig. 1e further confirm the formation of ultrathin nanosheets made of Co and Fe, perpendicularly embedded in the TiN matrix. Furthermore, two high-resolution STEM images with higher magnifications from one of the nanosheet regions from the cross-sectional and plan-view images are shown in Fig. 1c and Fig. 1f respectively. Based on the lattices measured and symmetry identified, it determines that the nanosheets in the view area are metallic $CoFe_2$ with a body-center-cubic (bcc) structure and a lattice constant of 2.86 Å, and furthermore form an epitaxy with the TiN matrix.

Of additional interest is that the "pillars" shape is rectangular in-plane (shown in plan-view images Fig 1d-f), i.e., thin sheet-like nanopillars, which is very different from the circular shape in the previously reported TiN-based VAN structures [20,21,44,45]. To understand the mechanism behind the nanosheet formation, we also investigated the stain states around the nanosheet using geometric phase analysis (GPA) based on a high-resolution STEM (HRSTEM) image. The color maps, ε_{yy} (Fig. 1g) and ε_{xx} (Fig. 1f), are generated with x direction perpendicular to the plate, and y direction parallel to the plate The strain maps are calculated with respect to the lattice plane spacings in the TiN matrix, with a displayed strain ranging from -30% to +30%. A high compressive strain exists in the nanosheet area (i.e., white contrast area) in the ε_{xx} mapping, but a relatively neutral strain (i.e., green contrast) in the nanosheet area in the ε_{yy}. This suggests the higher strain in the x-direction (normal to plate of the pillars) than that in the y-direction (parallel to plate of the pillars). This anisotropic in-plane strain can also explain the anisotropic rectangular shapes of the nanosheets observed which is to minimize the overall strain energy in the entire system, i.e., the longer edges present minimal strain (lattice-matched with the TiN matrix), while the shorter edges present large compressive strain to the TiN matrix. The anisotropic in-plane strain can also be confirmed by the intensity line profiles (Fig. S2 b1-b4) extracted from the plan-view HRSTEM image (Fig. 1f). Along the x-direction, the d-spacing of TiN and $CoFe_2$ phase are 2.12 Å and 1.43 Å separately which corresponds with a relatively large lattice strain of 32%. The lattice strain is relatively small along the y-direction because the two phases have comparable d-spacing (2.12 Å for TiN and 2.02 Å for $CoFe_2$). The in-plane orientation relationships can be identified as $CoFe_2$[100]//TiN[200] and $CoFe_2$[011]//TiN[020].

To further investigate the chemical compositions of the TiN-$CoFe_2$ nanocomposites, we conducted X-ray photoelectron spectroscopy (XPS) depth-profiling measurements by alternately sputtering material off the surface and measuring the freshly exposed surface with XPS. Before any sputtering, the surface shows that Fe, Ti, and Co are mostly in the oxide phase, which is expected for films having been exposed to air. It is interesting to note that, as shown in Fig. S3 c-d, after sputtering off the adventitious carbon and oxygen the metallic $CoFe_2$ is revealed to be the dominant species. However, it is noted that the small oxygen peaks remain below the top surface of the nanocomposite sample, which suggests the Co-O and Fe-O bonds remain in the nanocomposites. This is likely due to Co and Fe bonding to oxygen atoms at the nanosheet/matrix interfaces. The XPS shows the co-exitance of TiO_xN_y and TiN peaks in Ti 2p spectra in the matrix, indicating minor oxidation of TiN.

The microstructure tunability was realized by tuning laser frequency from 2 Hz to 10 Hz as shown in Fig. 2b and Fig. 2d. Since the $CoFe_2$ nanosheets have a rectangular-shape cross area, we analyzed the length distribution of the short edge and long edge respectively and plotted them in Fig. 2c and Fig. 2f. As laser frequency increases, the dimension of $CoFe_2$ nanosheets decreases significantly. The average dimension of $CoFe_2$ sheets in the 2 Hz sample is $7.39nm \times 30.61nm$, while it decreases to $3.14nm \times 16.73nm$ by increasing the laser frequency to 10 Hz. The tunability in dimension can be explained by the shorter adatoms diffusion time during the deposition process with higher laser frequency. Besides laser frequency, the temperature-dependent study provides another approach to effectively tune the microstructure of TiN-$CoFe_2$ thin films (Fig. S4). Clearly, as the temperature increases from

500 °C to 700 °C, the $CoFe_2$ nanosheet dimensions increase from $1.45nm \times 4.69nm$ to $7.39nm \times 30.61nm$.

The optical properties of the two-phase TiN-$CoFe_2$ nanocomposites were characterized by spectroscopic ellipsometry. The ellipsometry data ψ and Δ were collected on both 2 Hz and 10 Hz TiN-$CoFe_2$ films, and compared with two reference samples, i.e., a pure TiN film and a pure $CoFe_2O_4$ film. It is noted the reference single phase $CoFe_2O_4$ film was grown under vacuum condition, which may also have partial reduction and form $CoFe_2$ phase. To retrieve the dielectric permittivity, the data were fitted by applying general oscillator models. The real part of the dielectric permittivity (Fig. 3a) confirms pure TiN is metallic ($\varepsilon' < 0$) and pure $CoFe_2O_4$ film is dielectric ($\varepsilon' > 0$) for most wavelengths. Due to the anisotropic nature of two-phase VAN films, the permittivity of VAN films is fitted and plotted along out-of-plane ($\varepsilon_{\perp}$) in solid lines and in-plane ($\varepsilon_{||}$) in dashed lines, respectively. It is clear that the out-of-plane real permittivity($\varepsilon_{\perp}$) of both 2 Hz and 10 Hz samples is positive but very close to 0 throughout all the measured wavelengths, while in-plane real permittivity ($\varepsilon_{||}$) exhibits negative values throughout. The opposite sign in optical permittivity demonstrates a large Type-II hyperbolic dispersion regime (i.e., $\varepsilon_{\perp} > 0$ and $\varepsilon_{||} < 0$) as the shaded area in Fig. 3a). Considering the metallic $CoFe_2$, it is possible that the $CoFe_2$ phase could also contribute to the overall negative permittivity in-plane. The remaining small amount of oxygen containing phase at the surface and partial oxidation of TiN matrix near interface could both contribute to the overall positive permittivity out-of-plane. Note that the 10 Hz sample shows a larger negative value of $\varepsilon'_{||}$ compared to the 2 Hz one, suggesting that higher density of the nanopillars and more vertical interfaces present stronger optical anisotropy in the system. Fig. 3b plots the imaginary permittivity as a function of wavelength. Both the 2 Hz and 10 Hz samples show small optical losses along the out-of-plane direction because of their more dielectric nature compared to the TiN alone.

To further study the magnetic behavior of TiN-$CoFe_2$ nanocomposites, magnetization (M) vs. magnetic field (H) was measured in in-plane and out-of-plane directions at room temperature using Quantum Design SQUID-VSM. As shown in Fig. 4a, the out-of-plane hysteresis loops of 2Hz sample exhibits a saturation magnetization $M_{s\perp} = 329\ emu/cm^3$, and coercivity $H_{c\perp} = 1235\ Oe$, while the magnetization and coercivity along in-plane direction are only $M_{s||} = 257\ emu/cm^3$ and $H_{c||} = 708\ Oe$ respectively. The wider out-of-plane loop suggests a strong magnetic anisotropy with an out-of-plane easy axis, which result from the perpendicular elongated shape of $CoFe_2$(O) nanosheets. The magnetic behavior of 10Hz sample shows a similar trend, with smaller coercivity $H_{c\perp} = 771\ Oe$ and $H_{c||} = 367\ Oe$ (Fig. 4b). This can be explained by the smaller dimension of $CoFe_2$ nanosheets. Considering the possibility of coupling effect between plasmonic TiN and ferromagnetic $CoFe_2$, it is worth to study their magneto-optical (MO) coupling properties. Magneto Optic Kerr Effect (MOKE) measurements were conducted on both 2Hz and 10Hz samples under room temperature and the results are plotted in Fig. 4c-f. Polar MOKE was measured with a normal incident laser ($\lambda = 632.8\ nm$) and out-of-plane magnetic field, while a 30° laser and in-plane magnetic field were induced in longitudinal MOKE configuration. The obtained MOKE M-H loops indicate that a magneto-optical (MO) coupling effect presents in both two samples. The results show a similar trend with that characterized by VSM, i.e., very strong perpendicular magnetic anisotropy and tunable coercivity comparing the 2Hz and 10Hz samples. Furthermore, the 10Hz sample shows a larger Kerr rotation signal compared to the 2Hz sample, in both out-of-plane and in-plane directions. This can be explained by the enhanced coupling introduced by the higher density of TiN-$CoFe_2$ interfaces in the 10Hz sample compared to that in the 2Hz sample.

The overall characteristics of the new TiN-$CoFe_2$ hybrid metamaterial are the anisotropic $CoFe_2$ nanosheets formed in the TiN matrix, high epitaxial film quality, anisotropic optical and magnetic properties, as well as unique magneto-optical coupling properties. Compared to the TiN-Au, TiN-Ag, and TaN-Au systems previously demonstrated[19–21], TiN-$CoFe_2$ opens up the potential of highly anisotropic metamaterials designs, i.e., non-magnetic vs. strong magnetic. The unique magneto-optical coupling demonstrated at the TiN and $CoFe_2$ interfaces also presents opportunities in future designs of optical switchable spintronic devices and magnetic data storage devices. One of the major challenges is the interdiffusion between the oxide and the nitride in the system and the resultant reduction of the oxide phase. Selecting more stable oxides and minimizing interdiffusion by controlling the growth conditions will be critical for future exploration of nitride-oxide hybrid systems. Additional tunability can be achieved by other material combinations, novel three-phase system designs, and multilayer stacks of nitride-oxide VAN with other systems for integrated functionalities.

Conclusion

In summary, we have demonstrated self-assembled TiN-$CoFe_2$ nanocomposite thin films by using the one-step PLD technique. Microstructure characterizations by STEM and XPS show ultrathin nanosheets with metallic $CoFe_2$ phase growing vertically aligned in the TiN matrix. Both the deposition frequency study (2Hz, 10Hz) and temperature-dependent studies suggest effective tunability in the microstructure of the secondary phase as well as the resultant properties. Ellipsometry measurements reveal that the samples exhibit a Type-II hyperbolic dispersion in most optical wavelengths considering the highly anisotropic morphology of the TiN matrix, vertically aligned oxides between the TiN matrix and the $CoFe_2$ nanosheets. The magnetic hysteresis loops reveal obvious magnetic anisotropy owing to the highly aligned $CoFe_2$ nanosheets. The well-integrated plasmonic and ferromagnetic materials in the hybrid system enable a strong magneto-optical coupling effect at the pillar-matrix interfaces. This new nitride-based metamaterial design demonstrated in this study may provide new routes for processing of nitride-metal based nanocomposites with enhanced anisotropic structural and physical properties, towards future photonic devices and optical switchable spintronic devices.

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National Nuclear Security Administration under Contract No. DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Methods

Thin film growth

The TiN-$CoFe_2O_4$ target consists of pie-shape $CoFe_2O_4$ and TiN targets. The nanocomposite thin films were deposited on MgO (001) substrates in Neocera pulsed laser deposition chamber with a KrF excimer laser (Lambda Physik Compex Pro 205, $\lambda = 248$ nm). The substrates were heated and maintained at 700 °C during deposition and a high vacuum condition (2.0×10^{-6} mbar) was kept during deposition and cooling process.

Structural characterization

X-ray Diffraction

The $\theta/2\theta$ XRD scans were measured by a Panalytical X'Pert X-ray diffractometer with a Cu Kα1 radiation source ($\lambda = 0.15406$ nm).

Transmission Electron Microscopy

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) (under a high angle annular dark field mode (HAADF)) were taken on a Thermo Fisher Scientific (FEI) Talos F200X system with a point-to-point resolution of 1.6 Å. High-resolution STEM images were collected on an aberration-corrected FEI Titan microscope equipped with a high-brightness Schottky field emission electron source operated at 300 kV. A FEI TitanTM G2 80-200 STEM with a Cs probe corrector and ChemiSTEMTM technology (X-FEGTM and SuperXTM EDS with four windowless silicon drift detectors) operated at 200 kV was used for HAADF-STEM imaging and EDS analysis. A Digital Micrograph plug-in (DM 1.8.3 package, HRTEM Research Inc.) was used for geometric phase analysis (GPA). The cross-sectional TEM samples were prepared by a standard procedure, including manual grinding, polishing, dimpling and a final ion milling step (PIPS 695 precision ion polishing system, Gatan Inc.).

X-ray Photoelectron Spectroscopy

XPS was performed using a Kratos Axis Supra XPS system with a monochromatic Al Kα X-ray source. An initial spectrum was taken of the surface of every sample before a depth profile for 40 steps was performed with a gas cluster ion sputtering system at 10 keV 1000 clusters for 60 seconds with an incidence angle of 40° with respect to the horizontal direction. The size of the analyzed area was 110 μm x 110 μm while the sputtered size was 2 mm x 2 mm (rastered). Base pressure during analysis was 1.2 x10^{-9} torr and the electron emission angle was at 54.7° with an active charge neutralizer. XPS data was analyzed using CasaXPS software with the Kratos relative sensitivity factors set to F 1s at 1. The O 1s signal at 530.6 eV (MgO) was used as an internal reference for peak positions for all samples.

Optical characterization

Spectroscopic ellipsometry measurements were carried out with a spectroscopic elliposometer (J.A. Woollam RC_2) with variable angles (55°, 65°, and 75°) and spectrum range from 210 nm to 2500 nm. The real and imaginary part of permittivity were obtained by fitting ellipsometer parameters psi (Ψ) and Delta(Δ) with Gen-Osc model in CompleteEASE software. Transmittance spectra were measured on UV–vis-NIR absorption spectrophotometer (Perkin Elmer Lambda 1050).

Magnetic Characterization

The magnetic hysteresis loops were measured by a Quantum Design MPMS-3 SQUID Magnetometer with vibrating sample magnetometer (VSM) mode. The magneto-optic Kerr effect (MOKE) measurements were carried out by a home-built system equipped with a photoelastic modulator with two polar (P) and longitudinal (L) configurations. A laser with a wavelength of 632 nm was applied as a source light and the magnetic field was in the range of -3500 Oe to 3500 Oe for P-MOKE and -7000 Oe to 7000 Oe for L-MOKE separately.

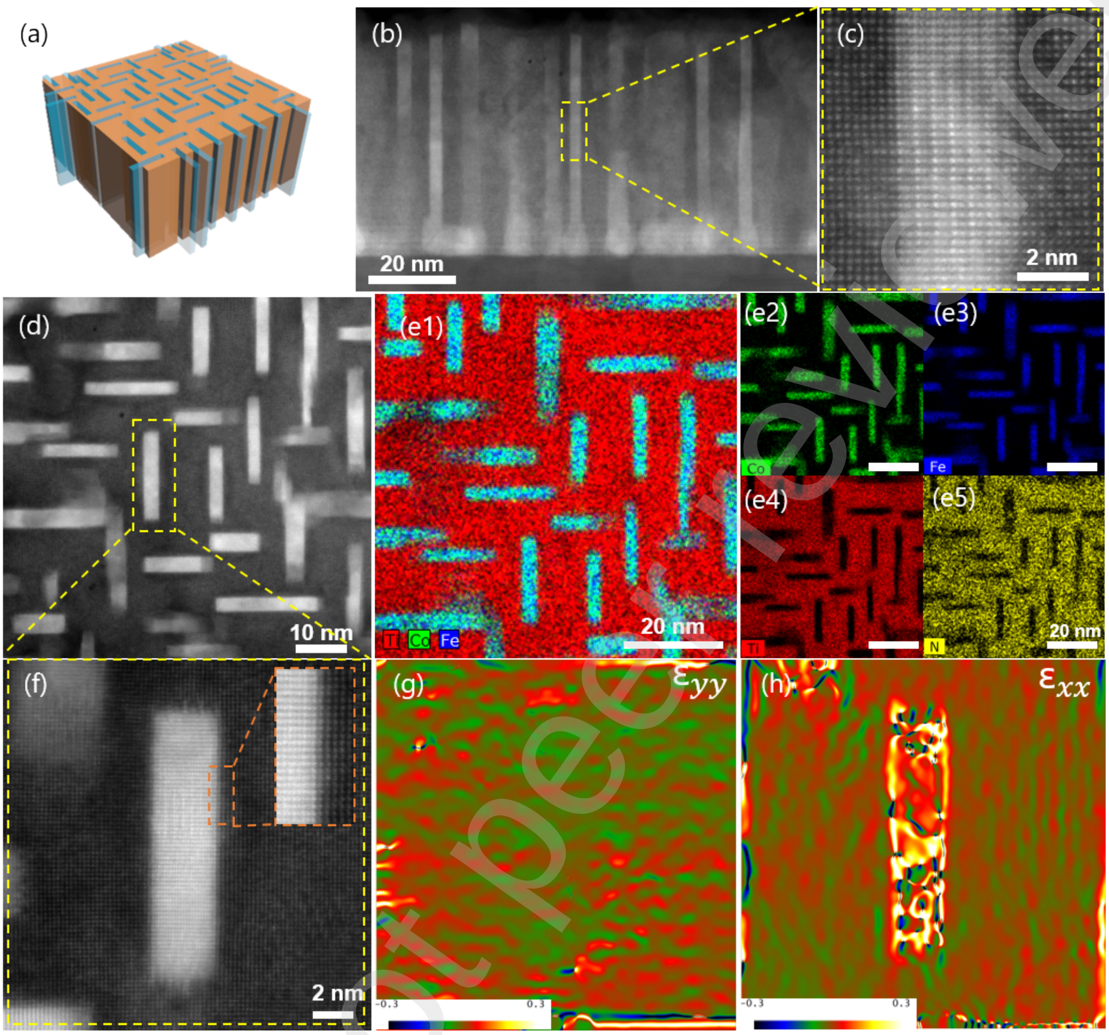

Fig. 1 | Microstructure of TiN-$CoFe_2$ nanocomposite thin film. (a) Schematic drawing of TiN-$CoFe_2$ microstructure; (b) Low magnification and (c) high magnification cross-sectional STEM images; (d) Plan-view STEM images with (e) corresponding EDS mapping of Co, Fe, Ti, N; (f) High-resolution STEM images of one nanosheet region with ε_{yy} strain mapping (g) and ε_{xx} strain mapping (h).

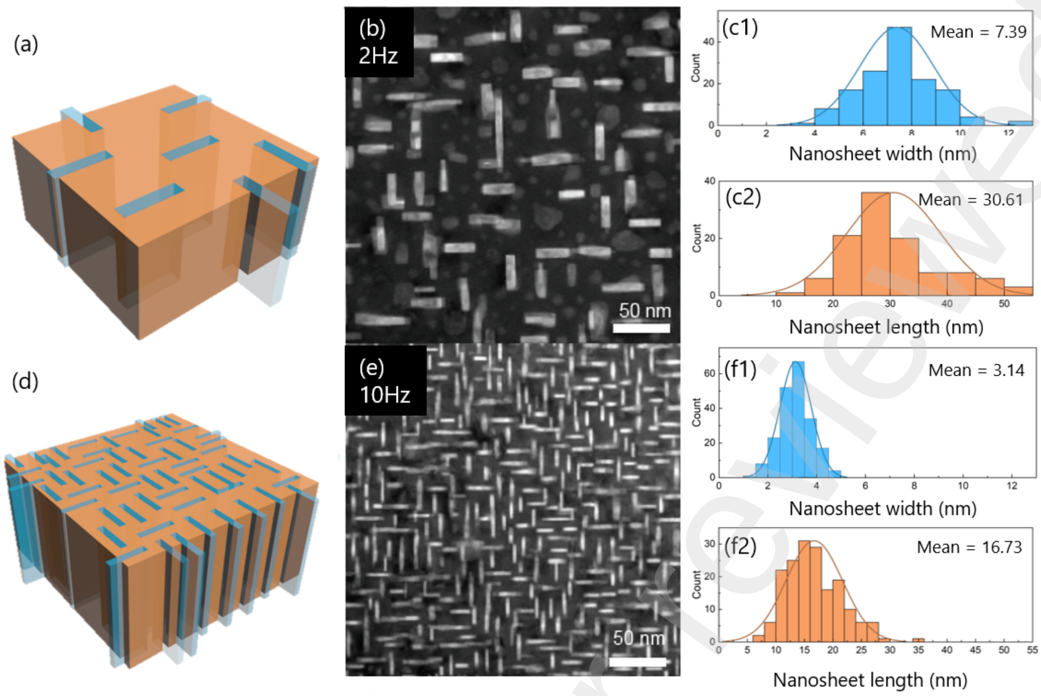

Fig. 2 | Microstructure turnability of TiN-$CoFe_2$ nanocomposite thin films. (a) Schematic drawing of 2Hz TiN-$CoFe_2$ VAN; (b) Plan-view STEM images of 2Hz TiN-$CoFe_2$ VAN; (c) Dimension distribution (short edge width and long edge length) of $CoFe_2$ nanosheets in 2Hz sample; (d) Schematic drawing of 10Hz TiN-$CoFe_2$ VAN; (e) Plan-view STEM images of 10Hz TiN-$CoFe_2$ VAN; (f) Dimension distribution of $CoFe_2$ nanosheets in 10Hz sample.

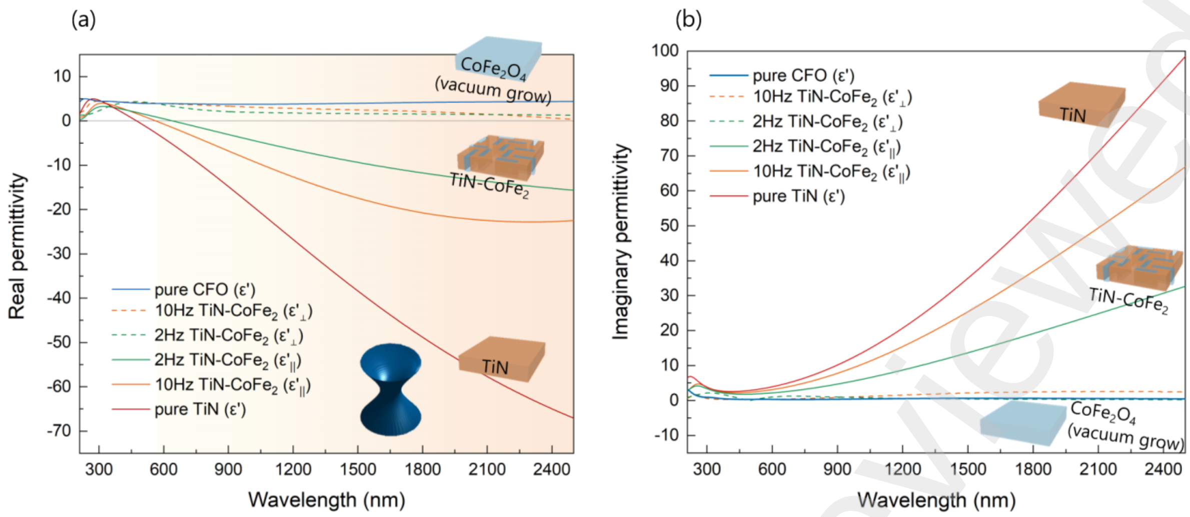

Fig. 3 | Optical properties of TiN-$CoFe_2$ nanocomposite thin films. (a) Real part and (b) imaginary part of permittivity of 2Hz TiN-$CoFe_2$, 10Hz TiN-$CoFe_2$, pure TiN, and pure $CoFe_2O_4$ sample.

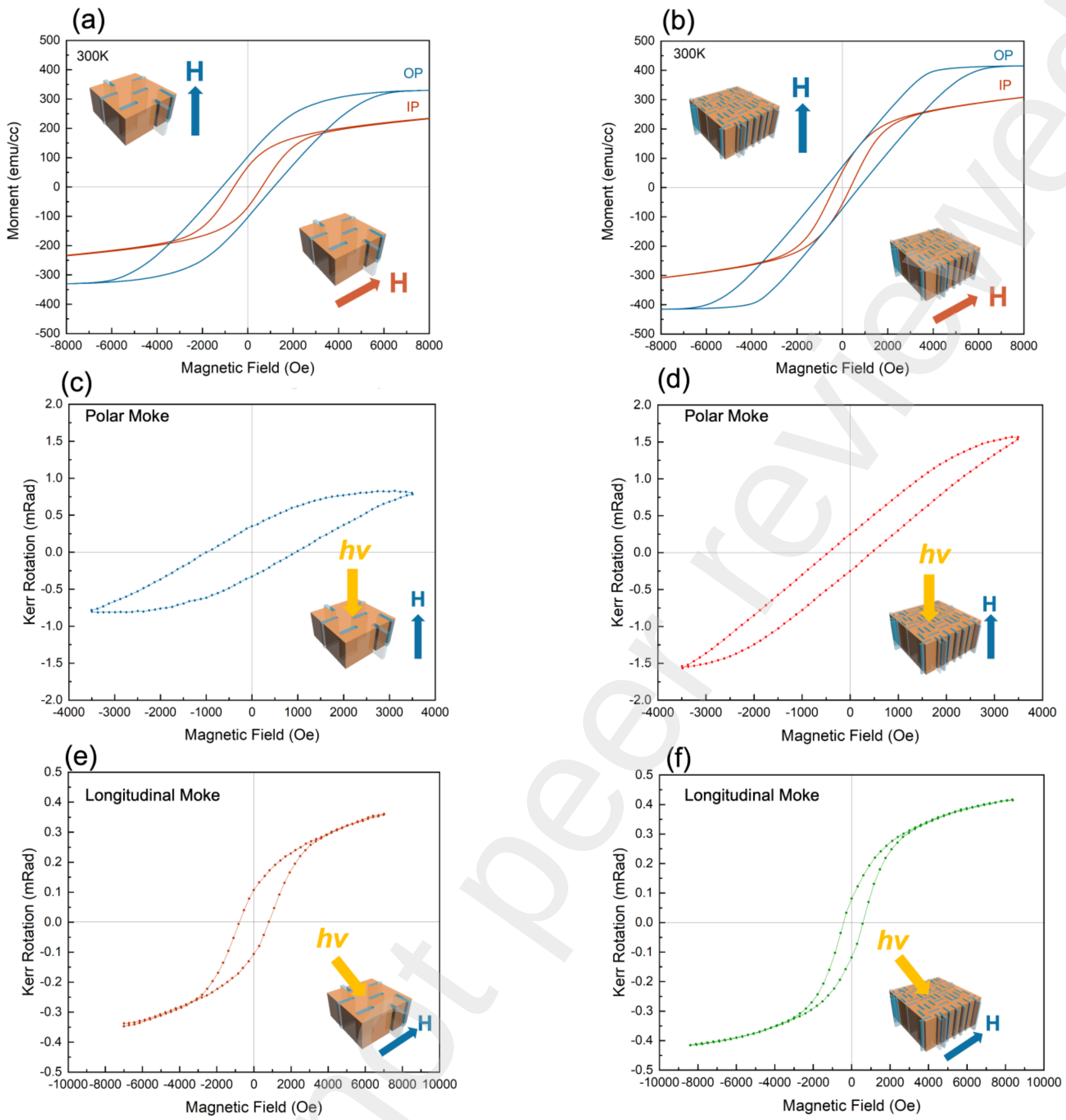

Fig. 4 | Magnetic properties and magneto-optical coupling effect in TiN-$CoFe_2$ nanocomposite thin films. (a) Comparison of in-plane and out-of-plane M-H hysteresis loops of 2Hz TiN-$CoFe_2$ nanocomposites; (b) Comparison of in-plane and out-of-plane M-H hysteresis loops of 10Hz TiN-$CoFe_2$ nanocomposites; (c) Polar and (e) longitudinal Kerr rotation of 2Hz TiN-$CoFe_2$ nanocomposites; (d) Polar and (f) longitudinal Kerr rotation of 10Hz TiN-$CoFe_2$ nanocomposites.

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