



# 2021「中技社科技獎學金」

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## Epitaxial Refractory Titanium Nitride (TiN) an Alternative Plasmonic Material for Energy Harvesting Applications



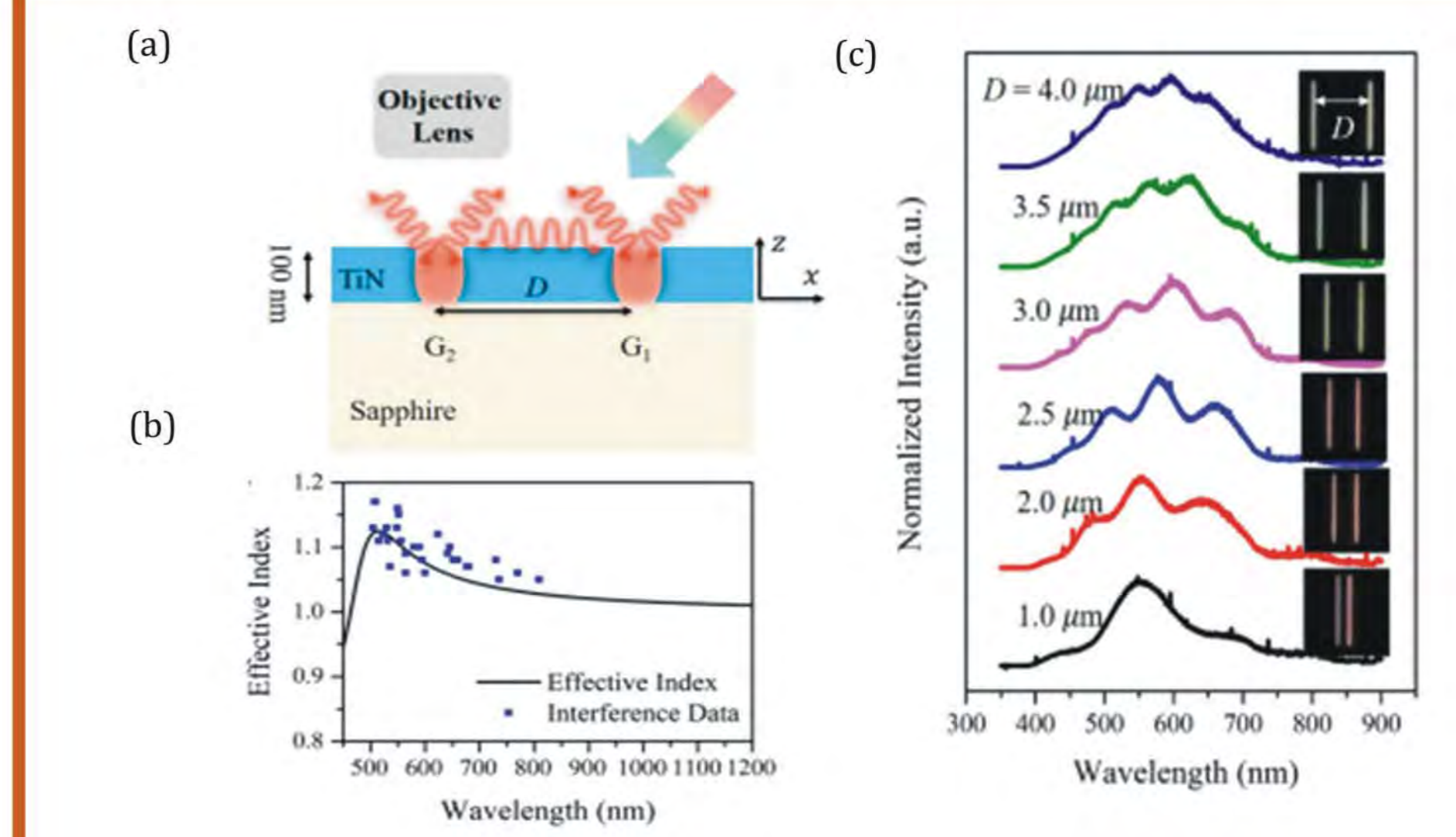
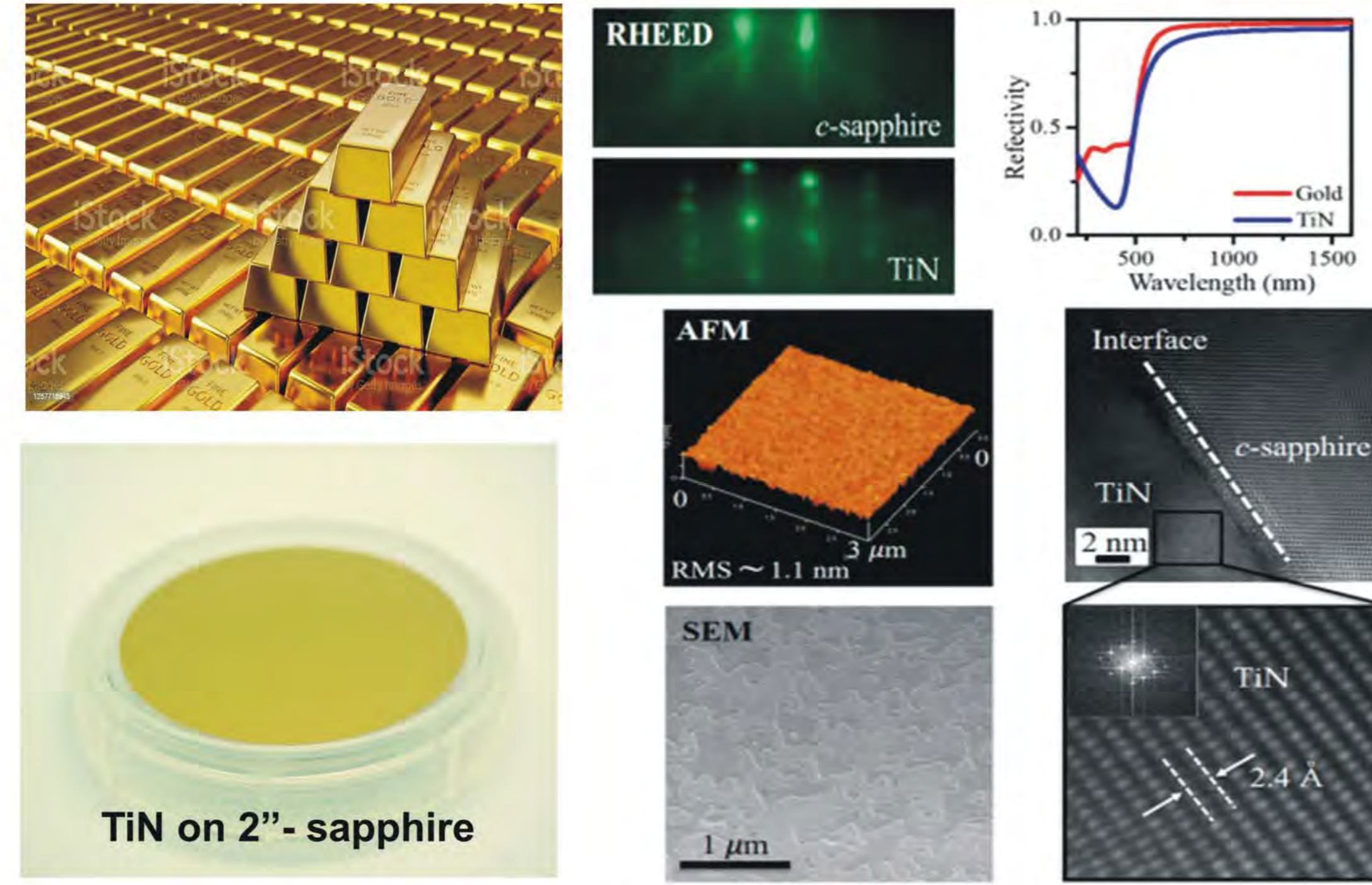
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### Abstract

We demonstrate a single-layer metasurface broadband absorber made from the oxidation-resistant TiN(111) epitaxial film grown on c-plane sapphire by nitrogen-plasma-assisted molecular beam epitaxy (MBE) with 90% absorptivity over the visible spectrum. Meanwhile, we have demonstrated refractory TiN/GaN heterostructures for hot carrier device applications. Alternative TiN has received less attention than other plasmonic materials (aluminium, silver, and gold) for photoexcited hot carrier applications, and its properties are unknown. Barrier height in TiN/p-GaN between the interface is determined via XPS analysis and Schottky barrier height in TiN/n-GaN is determined by the I-V curve. Consequently, the work function of TiN measured the Schottky barrier height of the TiN/p-GaN and TiN/n-GaN to explain the relative benefits and constraints of this hot carrier high power photodetectors. We concluded that using a p-type semiconductor for photodetection in visible regimes is a good approach for optoelectronic high power hot-carrier devices (space sciences) and plasmon-driven photocatalytic systems.

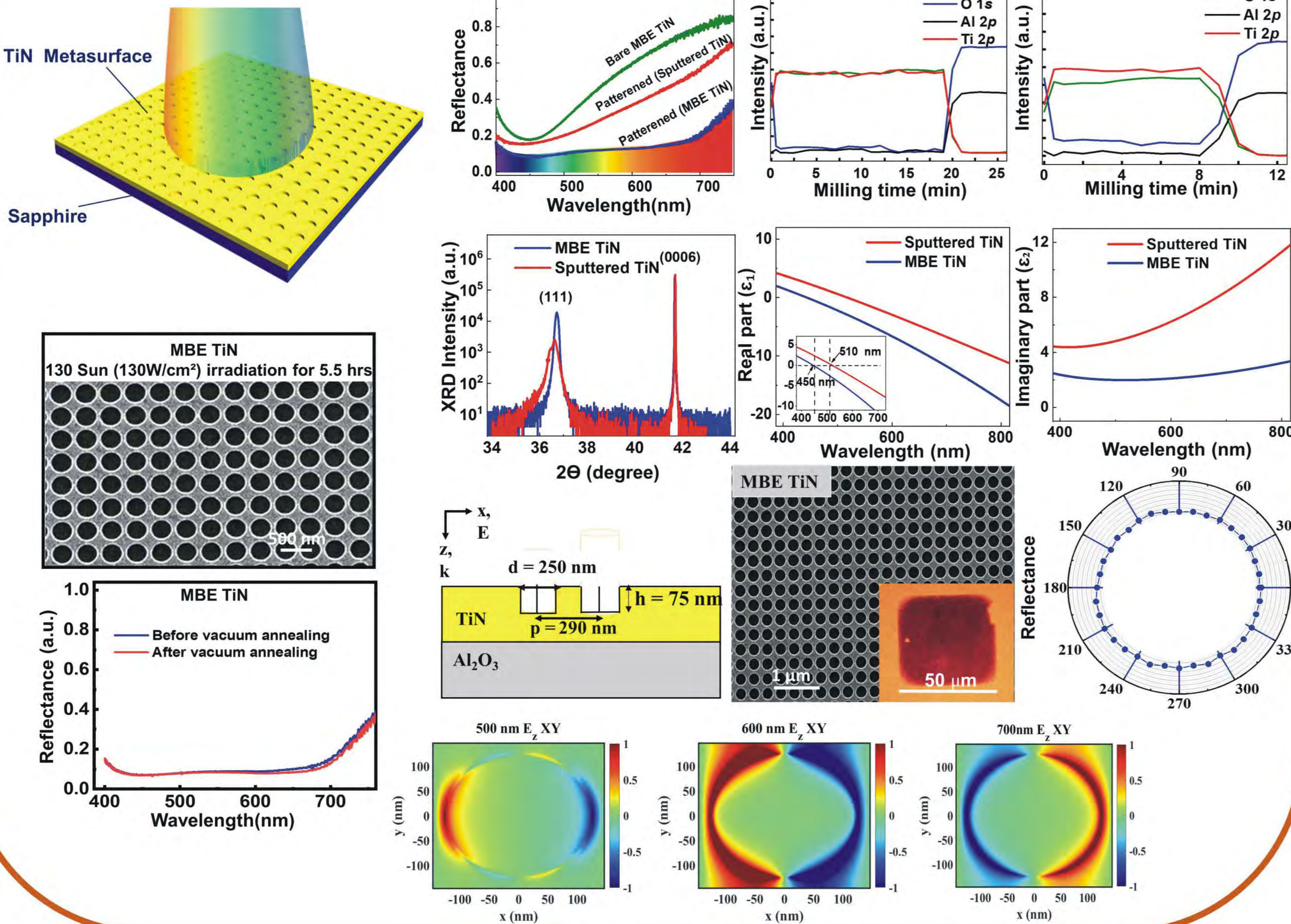
### Alternative to Gold (TiN) as plasmonic material



Surface plasmon polarization (SPP) interference using TiN surface Fabry-Pérot cavities. (a) Schematic of the white-light interference setup used for measuring the SPP interference patterns from TiN double-nanogroove surface cavities patterned by focused ion beam (FIB) milling with varying nanogroove distances. An oblique incident (75–80°) white light from a halogen lamp was used as the excitation source. (b) SPP interference patterns obtained from different double-nanogroove surface cavities. Corresponding dark-field optical images are shown in the insets. (c) Calculated effective index of SPP propagating at the TiN/air interface using the SE data. In comparison to the measured data from TiN nanogroove interference patterns (blue square dots). According to the SPP dispersion equation, the dielectric function of TiN measured by SE is used to determine the effective index ( $n_{eff} = \frac{\omega}{c} k_z$ ). The effective index is greater than one when the excitation wave frequency  $\omega < \omega_{sp}$  ( $\omega_{sp} = 470$  nm), which is consistent with the SE data.

### Optimized Titanium Nitride Epitaxial Film for Refractory Plasmonics and Solar Energy Harvesting

#### Result and discussion:



### Highly Stable Hot-Hole Induced Refractory TiN/GaN Photodetection

#### Result and discussion:

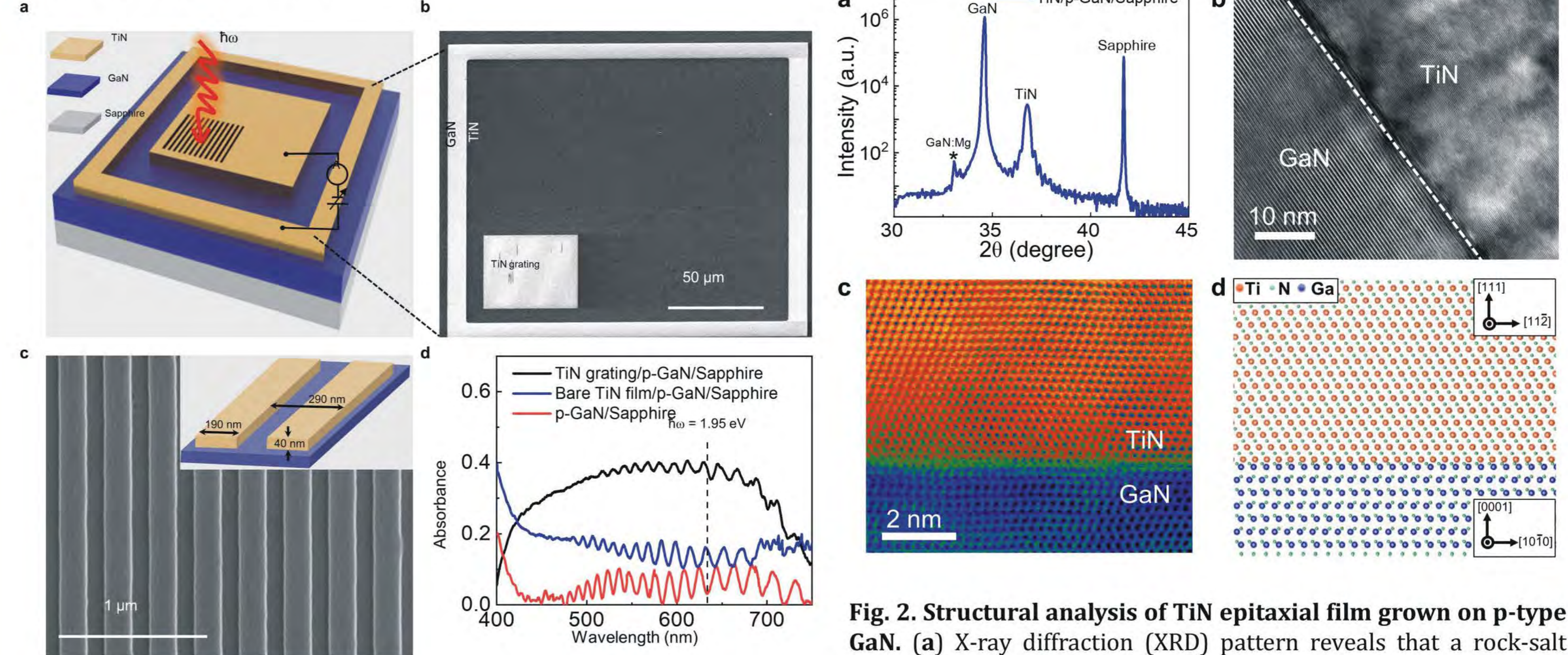


Fig. 2. Structural analysis of TiN epitaxial film grown on p-type GaN. (a) X-ray diffraction (XRD) pattern reveals that a rock-salt TiN(111) epitaxial film is grown on the p-type (Mg doped) GaN(0001)/sapphire(0001) wafer with two XRD peaks corresponding to wurtzite GaN (34.6°) and rock-salt TiN (36.6°). The FWHM values of GaN and TiN peaks are ~200 and ~500 arcsecond, respectively. (b) Transmission electron microscopy (TEM) image of TiN/GaN heterostructure illustrates the formation of abrupt interface between TiN and GaN and the thickness of the TiN layer is around 40 nm. (c) High-resolution TEM image of TiN/GaN projection along the [112] zone axis. The tensile strain in TiN film relaxes through a 20 (TiN)/19 (GaN) unit-cell match at the interface. (d) Schematic drawing shows the atomic arrangement of rock-salt TiN and wurtzite GaN crystal lattices.

Fig. 1. Optical energy-harvesting device made of TiN/p-GaN heterostructure. (a) Schematic design of the TiN/p-GaN device. (b) Scanning electron microscopy (SEM) image of as-fabricated TiN/p-GaN device. (c) SEM image of the grating structure patterned on TiN/p-GaN by electron beam lithography (the same structure is patterned on TiN/n-GaN for comparison). The TiN grating has 190-nm width and 40-nm height. The grating pitch is 290 nm. (d) Optical absorption spectra of TiN grating structure on p-GaN/sapphire, bare TiN film/p-GaN/sapphire, and p-GaN/sapphire substrate, showing the grating is designed to have the maximum absorbance at 1.95 eV (635-nm laser light).

Conclusion: In comparison with the TiN epitaxial film prepared by the reactive sputtering method, the XRD, SE, and XPS measurement results confirm that the MBE TiN epitaxial film has better crystalline and optical properties, as well as an oxygen-free stoichiometric composition. As an important consequence, the MBE TiN epitaxial film exhibits excellent thermal and chemical stabilities under high temperature annealing in vacuum and high solar irradiance, which make it a promising material for demanding high temperature applications such as solar thermophotovoltaics. Meanwhile when we compare the optoelectronic devices for the TiN/n-GaN and TiN/p-GaN. This novel heterostructure is for hot carrier plasmon induced photodetection for energy harvesting applications. The advantages with this combination both are refractory materials (TiN, GaN) and GaN is only one semiconductor which can be doped. Till now no one have reported this heterojunctions combinations and transitions metals nitrides for hot carrier photodetection is not well established. We have also induced a device phenomenon which is explaining the experimental results for TiN/p-GaN that phenomena is called photoconductive mode. As well as TiN/n-GaN device is the well-known Schottky behavior is represented. Perhaps this novel combination for hot carrier plasmon induced photodetection can be a potential tool for energy harvesting and space science and technology.

#### References:

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