Plasmonic Metamaterials: Looking beyond Gold and Silver

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Abstract

Conventional plasmonic devices have always used silver and gold as metallic components. Other areas of research such as metamaterials and transformation optics that rely on the plasmonic properties of materials also use noble metals as their metallic building blocks. However, these metals are not well-suited for many of the proposed device applications in the optical frequencies because of various problems, including large losses and nanofabrication issues. We show that alternative plasmonic materials such as transparent conducting oxides and transition metal nitrides overcome many of these challenges for metamaterial and plasmonic applications in the near-infrared and visible ranges.

1. Introduction

Whether it is the Lycurgus cup from ancient Roman times, or stained-glass windows of medieval cathedrals, plasmonics has always been associated with gold and silver [1]. Gold and silver have also been used as plasmonic elements in the more recent research areas including metamaterials (MMs) and transformation optics (TO) [2]. These noble metals have high DC conductivity, or equivalently low ohmic losses. However, the optical losses of these materials are not small owing to the excessive absorption arising from interband transitions [3]. Additional losses arise in these metals when they are patterned at the nanoscale; this is because nanopatterning often results in small grains, rough surfaces and semi-continuous films [3]. Aside from the issue of losses, another problem with metals is that their real permittivity values are too large in magnitude to be useful in many TO applications. Transformation optics applications typically require that the polarization responses of the dielectric and metallic components should nearly balance. This would require that the magnitudes of their real permittivities should be of the same order [3], but noble metals have very high carrier densities, which makes their real permittivities very large in magnitude. Furthermore, the optical properties of metals are not tunable, which makes the design of efficient devices difficult, and hence many plasmonic applications that require switching would not be possible with the use of metals. Finally, noble metals are not compatible with standard silicon nanofabrication technology. This is because noble metals diffuse into silicon to produce deep-level traps that substantially reduce carrier lifetimes. This undesirable effect means that noble metals cannot be easily integrated into standard silicon processes.

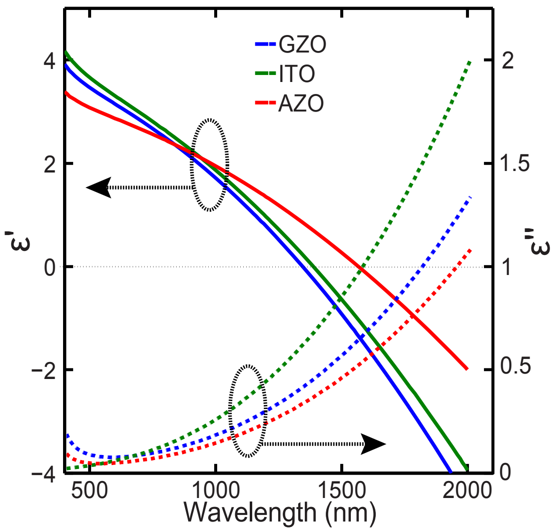

Fig. 1: Dielectric function of Al-doped ZnO (AZO), Ga-doped ZnO (GZO) and indium-tin-oxide (ITO) thin films retrieved by spectroscopic ellipsometry.

Many of these drawbacks of noble metals can be overcome with the use of alternative plasmonic materials (APMs). Different APMs are suitable in different operational wavelength ranges, and the available choices of APMs for a particular wavelength range depend on the carrier concentration supported by the material and the optical losses in the material. In the near-infrared range, transparent conducting oxides (TCOs) form good APMs [4]. These are formed by doping oxide semiconductors degenerately up to about 10^{21} cm^{-3}. However, TCOs have low carrier concentrations that are too low to be useful in the visible range. In contrast, transition metal nitrides (TMNs) are good APMs in the visible range. Transition metal nitrides are ceramics whose carrier concentrations can reach up to 10^{22} cm^{-3} [4]. These materials are compatible with semiconductor manufacturing processes and have properties can be changed significantly by changing the deposition conditions. Owing to many of these advantages, we have chosen to study the optical properties of TCOs and TMNs and their suitability for many plasmonic, MM and TO applications.

2. Transparent conducting oxides

Popular TCOs such as indium-tin-oxide (ITO) and heavily-doped zinc oxide are low loss APMs in the near-infrared range. These TCOs can be easily deposited by many techniques such as laser ablation and sputtering. We have adopted pulsed laser deposition (PLD) to deposit thin films of ITO, Ga-doped ZnO (GZO) and Al-doped ZnO (AZO) and study their optical properties. The optical properties are extracted by ellipsometry measurements (V-VASE, J.A. Woollam Co.) using a Drude-Lorentz model. The Drude portion of the model accounts for the free electron response, and the Lorentz portion accounts for the direct bandgap absorption in the near-ultraviolet. Figure 1 shows the dielectric functions of AZO, GZO and ITO films with the highest possible carrier concentrations. While ITO and GZO films show metallic properties for wavelengths longer than 1.3 µm, AZO shows metallic properties for wavelengths longer than 1.8 µm. The losses are the smallest for AZO and are about four times smaller than those in silver at similar wavelengths.

3. Transition metal nitrides

Among the many TMNs, we study the non-stoichiometric nitrides of Ti, Hf, Zr and Ta. Thin films of TMNs were deposited by DC reactive sputtering and optically characterized by spectroscopic ellipsometer (V-VASE, J.A. Woollam Co.). The optical dielectric functions retrieved for these films are as shown in Fig. 2. The nitride films are metallic for wavelengths longer than about 500 nm. The losses in TiN films are the lowest, followed by ZrN. TaN and HfN have higher losses, which might be partially alleviated by further optimizing the deposition conditions.

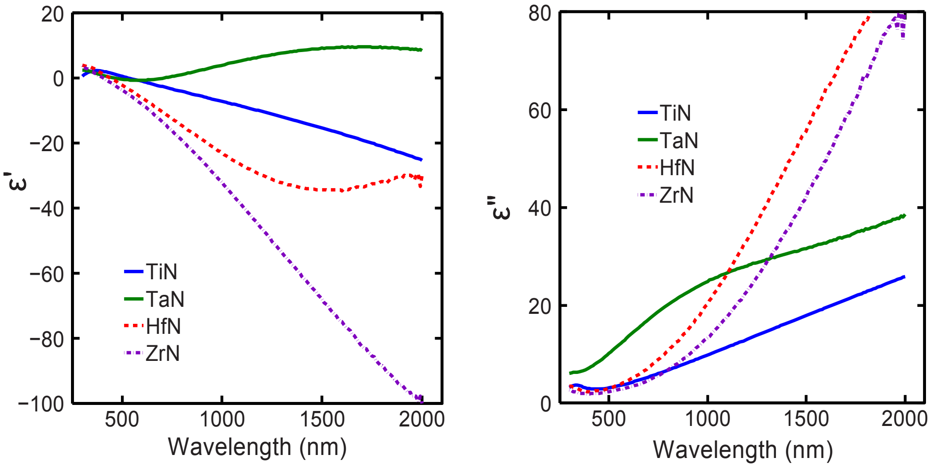

Fig. 2: Dielectric functions of sputter-deposited thin films of titanium, tantalum, zirconium and hafnium nitrides retrieved from spectroscopic ellipsometry.

3. Discussion

Plasmonics, MMs and TO devices make different classes of devices which have different requirements for high performance. Hence, different materials perform better in different applications. When considered plasmonic applications, TiN- and TCO nanoparticles enable strong localized surface plasmon resonances (LSPR) in the red end of the visible and in the near-infrared ranges, respectively. Simple nanoparticles (nanospheres) of gold or silver would not be able to produce LSPR in these wavelength ranges. Thus, APMs offer significant advantages in sensing and other applications where LSPR is used. Considering surface plasmon-polariton (SPP) waveguiding applications, calculations show that TiN and ZrN would perform nearly as good as gold, but worse than silver. Owing to problems such as the chemical stability of silver, TiN and ZrN could be promising substitutes for metals for SPP waveguiding applications. APMs outperform gold and silver by many orders of magnitude for non-resonant MMs such as hyperbolic MMs. However, there are specific applications such as negative-index materials (NIMs), where silver and gold remain the materials of choice [5]. In many other important MM applications such as TO devices, APMs can outperform the noble metals. Due to other advantages of APMs such as easier fabrication and integration, APMs are promising as good substitutes for metals in the optical frequency range.

4. Conclusion

We show that transparent conducting oxides and transition metal nitrides such as TiN can be good replacements for noble metals as plasmonic elements in the optical range for many MM and TO applications.

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