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Conductive nitrides: Growth principles, optical and electronic properties, and their perspectives in photonics and plasmonics

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ABSTRACT

The nitrides of most of the group IVb-Vb-VIb transition metals (TiN, ZrN, HfN, VN, NbN, TaN, MoN, WN) constitute the unique category of conductive ceramics. Having substantial electronic conductivity, exceptionally high melting points and covering a wide range of work function values, they were considered for a variety of electronic applications, which include diffusion barriers in metallizations of integrated circuits, Ohmic contacts on compound semiconductors, and thin film resistors, since early eighties. Among them, TiN and ZrN are recently emerging as significant candidates for plasmonic applications. So the possible plasmonic activity of the rest of transition metal nitrides (TMN) emerges as an important open question. In this work, we exhaustively review the experimental and computational (mostly *ab initio*) works in the literature dealing with the optical properties and electronic structure of TMN spanning over three decades of time and employing all the available growth techniques. We critically evaluate the optical properties of all TMN and we model their predicted plasmonic response. Hence, we provide a solid understanding of the intrinsic (*e.g.* the valence electron configuration of the constituent metal) and extrinsic (*e.g.* point defects and microstructure) factors that dictate the plasmonic performance. Based on the reported optical spectra, we evaluate the quality factors for surface plasmon polariton and localized surface plasmon for various TMN and critically compare them to each other. We demonstrate that, indeed TiN and ZrN along with HfN are the most well-performing plasmonic materials in the visible range, while VN and NbN may be viable alternatives for plasmonic devices in the blue, violet and near UV ranges, albeit in expense of increased electronic loss. Furthermore, we consider the alloyed ternary TMN and by critical evaluation and comparison of the reported experimental and computational works, we identify the emerging optimal tunable plasmonic conductors among the immense number of alloying combinations.

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1. Introduction

The recent emergence of plasmonics, the science and technology of metallic nanostructures interacting with light, is based upon the surface plasmon polariton (SPP) modes in planar surfaces and localized surface plasmon resonance (LSPR) in metallic nanoparticles [1–14], two unique phenomena that manifest exclusively at the nanoscale. As a result, plasmonics is one of the most characteristic examples of what is called 'nanotechnology' nowadays, despite being manifested since antiquity and theoretically explained since the early twentieth century [15,16]. Thus, plasmonics promise radical breakthroughs in electronic devices [17–24], biosensing [25–35], catalysis and photochemistry [36–45], solar energy harvesting [46–64], photodedection [65–74], optical storage of information [75–84], telecommunications [85–94] and metamaterials [95–99]. These applications are, in their turn, based on the high spatial resolution of SPP and LSPR, which is below the diffraction limit of light [7,82,100–103], the ultra-fast response of plasmonic systems [104–107], the maximized absorption and scattering of light [1,108], the elevation of the metal's electrons to a hot state [109–113], and more importantly the creation of extreme near-fields [114–119] that result in enhanced Raman and fluorescence signals of adjacent molecules [28,120–128] and the increased electron field emission probability [129,130] at the resonance wavelengths.

The most popular plasmonic metals are gold and silver due to their high conductivity and low dielectric losses (especially for Ag); the former due to its chemical inertness and stability and its facile surface functionalization by thiolates [131] and the later due to the absence of interband transitions in the visible spectral range rendering stronger and tunable LSPR throughout the visible spectral range, yet in expense of the feature size resolution (*i.e.* for Ag nanoparticles with LSPR in red the particles should exceed 100 nm [132]). However, their spectral tunability is limited (LSPR of Au or Ag nanoparticles cannot be extended to UV, and extension to IR would dictate size and shape compromises), their melting point is low, especially when in nanoparticle form [133,134], making them unstable for photothermal and hot electron devices, their conduction electron mobility is very low, and consequently they exhibit high conduction electron losses [135–137] and they both exhibit relatively high work function [138] minimizing the electron emission probabilities. Copper combines the drawbacks of gold (interband absorption and dielectric losses in the visible) and silver (reactivity), its plasmonic behavior is inferior [139] and, consequently, studies on its plasmonic response are less frequent [140–143].

In order to tackle the aforementioned obstacles of gold, silver and copper, a quest for alternative plasmonic conductors is taking place recently [136,137,144–176]. Group-III metals (aluminum, gallium and indium) have been investigated for extending the plasmonic devices to the UV range [148–157]; however they suffer from fast oxidation resulting in a metal/oxide core/shell structures, which eventually operate in the visible spectral range [148]. In addition, they have exceptionally low melting temperatures (Ga nanoparticles melt even below room temperature) and high diffusivities that compromise their long-term stability. On the other hand, for extending the operation of plasmonic devices to IR, transparent conductors, such as indium tin oxide (ITO), aluminum-doped zinc oxide (AZO) and gallium-doped zinc oxide (GZO) have been implemented [158–169].

An emerging category of alternative plasmonic materials is the conductive transition metal nitrides (TMN), such as TiN, ZrN and TaN [169–183]. Going beyond the three aforementioned nitrides, of significant technological importance are all the nitrides of the transition metals of the group IVb-Vb-VIb (4–6 IUPAC) of the periodic table of elements, as shown in the reduced periodic table of elements in Fig. 1 (data taken from [184–187]); these nitrides can form cubic rocksalt-type crystals (B1-structure, Fm3m symmetry) and constitute a category of very important technological materials due to their exceptional mechanical properties, high melting point, refractory character and chemical stability over hostile environments. Thus, TMN are widely studied and used for a variety of applications, such as decorative coatings, protective and anti-corrosive coatings, in cutting tools and machining equipment; therefore, the works dealing with comparisons on their growth and properties are numerous and well-established [184,188–200]. They also exhibit electronic conductivity due to the partially filled valence *d* orbitals that are not completely hybridized with the N-2p electrons, as we will show below. The unique combination of their electronic properties with their stability and refractory character resulted in TMN being used also for applications in electronics, such as diffusion barriers [201–210], Schottky contacts [211–213], superconducting devices [214–219], conductive growth templates for wide bandgap semiconductors [220–222], field emission cathodes [223], and Ohmic contacts for optoelectronic devices [176,184,224] or other types of metallizations [225–231]. Finally, an exceptional asset is their compatibility with CMOS technology, due to their high electron mobility and refractory character [232–235], which enables their easy integration and upscaling in realistic, mainstream electronic devices. In this respect, TMN would boost the integration of plasmonics into CMOS technology for optical communications by replacing the incompatible Au [236] and Ag [237]. Alloying elements to form conductive ternary compounds in the B1 rocksalt structure include the elements of the groups II, IIIa, and IIIb (mostly Al).

In this work we review the fundamental properties (phases, microstructure, growth techniques) of the TMN, as well as their electronic structure via detailed *ab-initio* and semi-empirical computational methods, their dielectric function spectra extracted from an extended literature survey of reported ellipsometry and optical reflectivity spectra. As a result, we critically compare the reported electronic properties (such as resistivity/conductivity, conduction electron density-via the unscreened plasma energy, the spectral position of their interband transitions and their work-function). We also consider the effect of grain size to the optical and electronic properties of TMN.

Furthermore we consider the successful alloying of TMN to form ternary TMN (or more accurately pseudobinary nitrides, because the B1 structure is retained in the entire compositional range and the nitrogen sublattice of the B1 structure remains intact during