Complex conducting nitrides: Synthesis, structure, properties and applications

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ABSTRACT: The combination of electrical conductivity, chemical and metallurgical stability, refractory character and lattice constants close to those of III-nitrides make transition metal nitrides promising candidates for electronics and device applications. We study the structure, stability and the plasma energy (or conduction electron density) of stoichiometric, transition metal nitrides of similar crystal quality as well as of the widest variety of ternary transition metal nitrides of rocksalt structure ever reported. We identify the factors, which determine the lattics constant of the ternary nitrides. We establish the phase spaces of the plasma energy (6.9-10.5 eV) and the work function (3.7-5.1 eV) of these complex nitrides with their lattice constant (0.416-0.469 nm) and we investigate the limits of their applications.

I. INTRODUCTION

The nitrides of group IVb-VIb transition metals (TMN) exhibit a unique combination of significant electron conductivity, refractory character, high hardness, chemical inertness and a cubic rocksalt structure with a lattice constant close to those of III-nitrides. These properties make them suitable for applications in electronics [1-4]. However, TMN's electronic properties should be combined with the lattice constant in order to match the substrate's lattice and prevent device's degradation and failure due to the formation of misfit dislocations [3]. Therefore, conducting ternary nitrides with tailored lattice constant can be very promising candidates replacing the currently used TiN and TaN [5-7]. In this work we review the ternary nitrides $Ti_xMe_{1-x}N$ and $Ta_xMe_{1-x}N$ (Me=Ti, Zr, Hf, Nb, Ta, Mo, W) over the whole x range ($0<x<1$) grown by Pulsed Laser Deposition (PLD), Dual Ion Beam Sputtering (DIBS) and Dual Cathode Magnetron Sputtering (DCMS). We investigate the validity of Vegard's rule and the effect of growth-dependent stresses to the lattice constant. Finally, we present the correlations between their lattice constant and the work function (*WF*) and the plasma energy E_p.

II. EXPERIMENTAL DETAILS

Ternary $Ti_xMe_{1-x}N$ and $Ta_xMe_{1-x}N$ films, 200-300 nm thick, were grown on Si{001} by reactive Pulsed Laser Deposition (PLD) using the 2^{nd} harmonic of a Nd:YAG laser in flowing N_2 ambient. The sample composition x was changing by using mixed Ti-Me and Ta-Me targets of varying fractions. $Ti_xTa_{1-x}N$ films have been also grown by DIBS and DCMS. The composition of the films was determined by *in-situ* Auger Electron Spectroscopy (AES). The crystal structure was investigated by $\theta-2\theta$ X-Ray Diffraction (XRD) in Bragg-Brentano geometry using the CuKα monochromatized line.

III. RESULTS AND DISCUSSION

The XRD patterns of all the studied films exhibited exclusively the characteristic (111) and (200) peaks of the rocksalt structure for all cases without any fine structure, indicating perfect solid solutions over the full range of x ($0<x<1$) for all cases, demonstrating the general property of TiN and TaN being fully miscible in every MeN of rocksalt structure, independently of the phase diagram of the constituent metals. The bonding of the metal's *d* valence electrons with the nitrogen's *p* electrons [5] makes possible the formation of any rocksalt ternary nitride of the group IVb-VIb metals regardless the valence electron configuration.

The cell sizes (α) were calculated from the (111) interplanar spacings and are displayed in Figs. 1,2. The α vs. the composition x for a very wide variety of $Ti_xMe_{1-x}N$ and $Ta_xMe_{1-x}N$ (Me=Ti, Zr, Hf, Nb, Ta, Mo, W) follow distinct straight lines resembling (but not coinciding) Vegard's rule. In all cases, presented in Fig. 1, the α is expanded compared to the expected values from Vegard's rule; this is exclusively due to in-plane compressive stresses. The amount of stress is process-dependent (see Fig. 2). Thus, values of α for DIBS-grown $Ti_xTa_{1-x}N$ films are more expanded compared to those for PLD-grown $Ti_xTa_{1-x}N$ films due to excessive stress attributed to the contribution of energetic backscattered Ar neutrals. AES spectra revealed that Ar exists in the DIBS-grown films in addition to Ti, Ta and N. AES spectra from a PLD- and a DIBS-grown film, before and after annealing, exhibiting Ta (170-180 eV), Ti and N (360-420 eV) patterns are shown in Fig. 3; the DIBS sample also exhibits the Ar_{LMM} pattern (220 eV), resulting from the entrapment of backscattered Ar reflected from the target surface. After vacuum annealing at 850^oC for 3 hours the stress of the films is almost completely relieved and the Ar_{LMM} pattern reduces down to the detection limit of AES, indicating a strong outdiffusion of Ar.

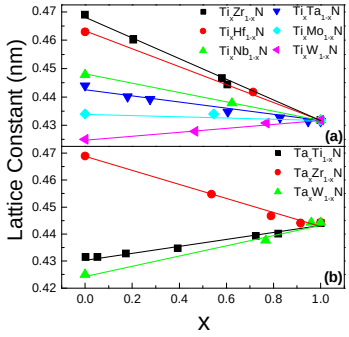

Fig. 1: Experimental demonstration of Vegard's rule for (a) Ti-based, and (b) Ta-based nitrides grown by PLD.

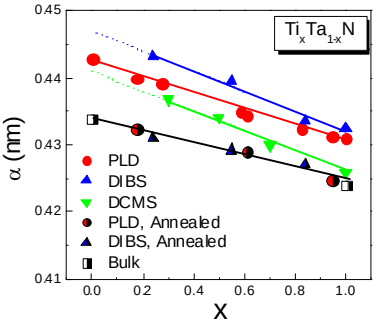

Fig. 2: Variation of the lattice constant with the composition x for ternary $Ti_xTa_{1-x}N$ grown by various techniques.

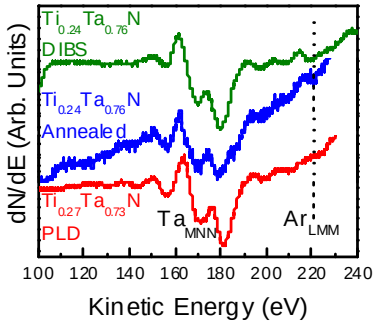

Fig. 3: AES spectra (Ta_{MNN} and Ar_{LMM} peaks) from $Ti_xTa_{1-x}N$ films grown by DIBS (and after annealing) and PLD.

The optical properties were studied using optical reflectance spectroscopy (ORS) and Spectroscopic Ellipsometry, which revealed the typical behavior of conductors, characterized by the plasma energy E_p, which is directly correlated with the conduction electron density N: $E_p = \hbar\sqrt{\frac{Ne^2}{\varepsilon_o m^*}}$. The phase space of E_p^2 with the nitride's lattice constant has an triangular shape with TiN, ZrN and WN being at the vertices. The form of this phase space reveals that $Ti_xZr_{1-x}N$ is the most versatile system for low-mismatch growth on various semiconductors since it exhibits almost constant E_p^2 (i.e. conduction electron density) and varying lattice constant in the vast range of 0.432-0.469 nm.

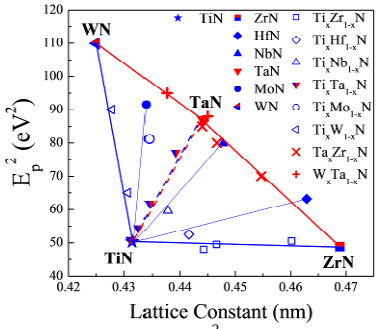

Fig. 4: The phase space of E_p^2 (which is proportional to conduction electron density) vs. the nitride's lattice constant.

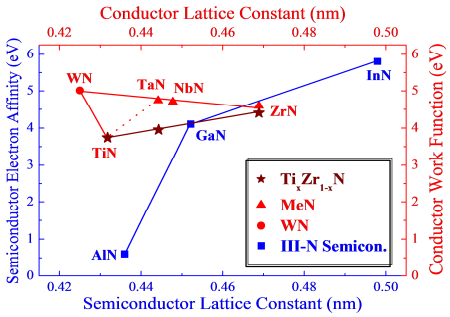

Fig. 5: The variation of *WF* with the nitride's lattice constant in comparison with the electron affinities and the lattice constants of III-nitrides from (Refs 7,8).

A very important factor for ohmic behavior of a contact is the *WF* of the conductor. *WF* values of selected $Ti_xZr_{1-x}N$ samples have been determined by *ex-situ* Kelvin probe measurements and are presented in Fig. 5 along with the values of binary nitrides from Ref. [8], as well as the electron affinities and lattice constants of III-nitride semiconductors. It is evident that $Ti_xZr_{1-x}N$ is structurally and electrically appropriate as growth template or ohmic contact for *n*-type $In_yGa_{1-y}N$. Taking into account the bandgap values of the III-nitride semiconductors, $W_xTa_{1-x}N$ might be also promising as contact on *p*-type $Al_yGa_{1-y}N$.

In conclusion, conducting, ternary TMN are stable in the rocksalt structure independently of the valence electron configuration of the two constituent metals and the crystal structure of the constituent binary nitrides. They exhibit a vast range of lattice constants, plasma energy (i.e. conduction electron density) and *WF* making them suitable for various electronic applications.

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