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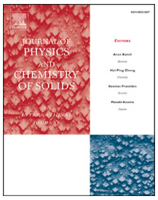

Coherent assembly of heterostructures in ternary and quaternary carbonitrides

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ABSTRACT

In this study, ternary and quaternary carbonitride heterostructure systems were grown on silicon (100) substrates in order to investigate coherent assembly in TiCN/TiNbCN. The heterostructure films were grown using the reactive r. f. magnetron sputtering technique by systematically varying the bilayer period (Λ) and the bilayer number (n), while maintaining a constant total coating thickness (~3 μm). The heterostructures were characterized by high angle X-ray diffraction (HA-XRD) and low angle X-ray diffraction, while the TiCN and TiNbCN layers were analyzed by X-ray photoelectron spectroscopy and transmission electron microscopy. The HA-XRD results indicated preferential growth in the face-centered cubic (111) crystal structure for the [TiCN/TiNbCN]n heterostructures. The maximum coherent assembly was observed with the presence of satellite peaks. Thus, ternary and quaternary carbonitride films were designed and deposited on Si (100) substrates with bilayer periods (Λ) in a broad range from nanometers to hundreds of nanometers in order to study the structural evolution and coherent assembly progress as the bilayer thickness decreased. We determined physical properties comprising the critical angle (θc) (0.362°), electronic density (ρe) (0.521 × 1033 el/m^3), dispersion coefficient (δ) (0.554 el/m^3), and refractive index (n) (0.999944) as functions of the number of bilayers (n).

1. Introduction

Nanostructure heterostructure materials have attracted much research interest because the nanometer scale may drastically change the density of the electronic states and the optoelectronic properties of semiconductors [1]. Previous studies have shown that the strain-driven self-assembly of nanostructures is an inexpensive and effective manufacturing process, which has been investigated extensively over the past decade. However, tuning the size distribution and spatial ordering of these structures is still a challenge. Metals/ceramics are among the model materials used for investigating the self-organization of nanostructures in semiconductors as well as heterostructures with mechanical applications. Thus, Si/TiCN islands may be formed on a (1 0 0)-oriented Si substrate via self-organization due to the lattice mismatch between the deposited material and the substrate [2]. Isostructural heterostructure systems comprising metal/ceramic and ceramic/ceramic superlattices have attracted much attention because these combinations can have high hardness values, which are often 100% higher compared with the rule-of-mixture values, while they also retain good physical properties. Thus, many metal/ceramic and ceramic/ceramic films have been studied in the last 10 years, including Ti/TiN [3], BCN/CN/BN [4], and TiN/TiCN [5]. Many studies have reported the physical characteristics such as the electronic density (ρe), refractive index (n), and dispersion coefficient (δ), where they showed that these variables are highly dependent on the number of layers [6–9]. However, few studies have focused on the structural changes in ternary and quaternary carbonitride heterostructures. Therefore, in the present study, we designed TiCN/TiNbCN multilayered films with a total thickness of ~3 μm, which were deposited on Si (100) substrates with bilayer periods in a broad range from nanometers to hundreds of nanometers. We studied the structural evolution with decreasing bilayer thickness (Λ) in the TiCN/TiNbCN multilayered films and its relationship with coherent assembly as function of the correlation length in order to assess their possible technological applications in processes that require high performance.

2. Experimental details

Ternary and quaternary carbonitride heterostructures were grown on Si (100) substrates by using a multi-target magnetron sputtering system with an r. f. source (13.56 MHz). The plasma cleaning procedure was

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used for all of the substrates under an argon atmosphere.

The sputtering targets for titanium carbide and niobium used in this study were purchased from Kurt J. Lesker Company. The silicon substrates were purchased from NanoInk Company, and Ar and N_2 gases were obtained from AGA FANO S.A. Company. The two stoichiometric TiC and Nb targets both had diameters of 10 cm and purity of 99.99%. The deposition parameters used comprised a sputtering power of 400 W for TiC and 350 W for the Nb target, with a substrate–target distance of 7 cm, substrate temperature of 300 °C, and the substrate was subjected to circular rotation at 60 rpm to facilitate the formation of the stoichiometric quaternary film, which is necessary for obtaining the face-centered cubic (FCC) crystal structure. The substrate used in this study had a disk-type geometry with a diameter of 1 cm. The sputtering gas was a mixture of Ar (50 sccm) and N_2 (16 sccm) with a total working pressure of 6×10^{-3} mbar. An unbalanced r. f. bias voltage was applied, which generated a negative signal fixed at −50 V. Moreover, it was possible to vary the bilayer number among 1, 30, 50, 70, 150, and 200, where this effect changed the bilayer period due to the increase of the bilayer number for coatings with a constant thickness. X-ray diffraction (XRD) analysis was performed for the heterostructures in high-angle and low-angle ranges with a Bragg–Brentano configuration (θ/2θ), where the crystal structure was analyzed by using a Philips-MRD diffractometer with Cu-Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) was employed to analyze the carbonitride materials in order to determine their chemical compositions and the bonding of the titanium, niobium, nitrogen, and carbon atoms using an ESCAPHI 5500 system with monochromatic Al-Kα radiation and a passing energy of 0.1 eV. The surface sensitivity of this technique is very high and any contamination can produce deviations from the real chemical composition. Thus, exhaustive XPS studies were performed for the TiCN and TiNbCN films because XPS analysis is usually performed under ultrahigh vacuum conditions with a sputter cleaning source to partially remove undesired contaminants. Ti is highly reactive so the XPS analysis was conducted in an ultra-high vacuum region (low pressure 1×10^{-9} mbar), which means that it was necessary to have sufficient time for recording the XPS spectra. Low-angle XRD (LA-XRD) or X-ray reflectivity (XRR) scans allowed the characterization of the preferred orientations related to the growth direction. The bilayer periods in the multilayers were measured based on LA-XRD (θ/2θ) scans and they were compared with those obtained from transmission electron microscopy (TEM) micrographs. The structural assembly of the multilayered coatings was analyzed by TEM using a Philips CM30 microscope operating at 300 kV and by simulations of low-angle XRD patterns using Parratt's formalism [10]. The software used to simulate the low-angle XRD patterns using Parratt's formalism was ReMagX. ReMagX calculates and fits the specular X-ray reflection from a thin film sample by considering the magnetic contributions. This program can simulate standard non-magnetic XRR for variable energies based on Parratt's formalism. However, the real aim and strength of ReMagX is simulating the reflectivity from a multilayer material under circular polarized X-rays by calculating the specular reflection of a transition metal sample.

3. Results and discussion

3.1. HA-XRD analyses of heterostructure systems

The measured total thickness of the deposited $[\mathrm{TiCN/TiNbCN}]_n$ heterostructures was approximately 3 μm in all cases. The individual thickness varied as a function of the bilayer number from n = 1 to n = 200 to produce layers with thicknesses ranging from 1.5 μm to 15 nm, respectively. Fig. 1a shows the high-angle XRD (HA-XRD) patterns corresponding to the $[\mathrm{TiCN/TiNbCN}]_n$ multilayers, which indicates that there was a clear change in the diffraction patterns obtained for this set of multilayers as the bilayer period decreased. As shown in Fig. 1, with large bilayer periods, there was a clear preference for an FCC (111) orientation in both the Ti—C—N and Ti—Nb—C—N layers, where this preferential orientation was generated by the large number of crystallites that diffracted in that direction [11]. Therefore, the layer textures of Ti—C—N and Ti—Nb—C—N in the TiCN/TiNbCN multilayers remained constant with the (111) preferred orientation from the bilayer period with a thickness of 3 μm to the bilayer period with a thickness of 15 nm. In the thickest bilayer pattern, there were still some small contributions from Ti—C—N (200), Ti—C—N (220), and Ti—Nb—C—N (200) reflections, but they disappeared from the larger bilayer periods to the thinnest period heterostructures (Λ ≤ 15 nm), where the presence of a small peak in the (222) direction was associated with the intense (111) reflection peak. Thus, as the thickness of the individual layers decreased, the textured growth of each layer with respect to another increased. Therefore, the crystallites within the layer were increasingly coupled with respect to the crystals in the other layer because as the layer thickness decreased, the time required to generate their own preferential growth was reduced and this induced cube-on-cube assembly to generate monocrystalline growth. Thus, the monocrystalline growth increased the preferential peak intensity in the (111) direction, thereby decreasing the presence of the (200) and (220) peaks.

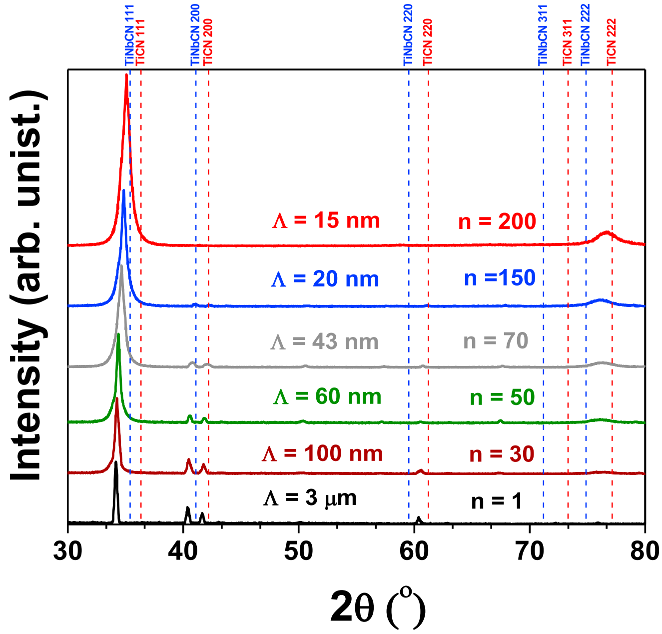

Fig. 1. HA-XRD patterns obtained for TiCN/TiNbCN heterostructures films deposited on Si (100).

The Ti—Nb—C—N (111) peak position exhibited a great deviation from the bulk value, which indicated possible stress evolution in the TiCN/TiNbCN layers with the bilayer period. The quasi-relaxed position observed for the thinner bilayer periods shifted progressively to higher compressive stress values as the bilayer period increased up to Λ = 1.5 μm. For the thinner period multilayers (n = 200), an abrupt change in the Ti—Nb—C—N (111) peak position was observed, which indicated stress relief due to the movement of this peak toward higher angles compared with the other multilayers but close to the bulk value (36.66°). The stress evolution for the (111) peak position in the XRD patterns was accompanied by progressive and intense symmetrical enlargement according to the increase in the intensity peak. Moreover, the patterns clearly showed that the widening peaks were reduced as the bilayer number decreased and the thickness of the individual layers increased [12,13]. Therefore, the residual stress in the layer could be estimated using Stoney's model by considering that the thickness of the layer was much less than that of the substrate [14]. In addition, the stress relief of around 80% can be explained by the presence of interfaces within the multilayer system and their increasing influence as the number of layers increased, where the two materials with equal crystalline