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Determination of superlattice effect on metal–ceramic nano-structures

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ABSTRACT

Binary nitrides multilayer systems were grown on silicon (100) substrates with the aim to study the coherent assembly in HfN/VN material. Multilayers films were grown via reactive r.f. magnetron sputtering technique by systematically varying the bilayer period (Λ) and the bilayer number (n) while maintaining constant the total coating thickness (~2.4 μm). The layers were characterized by high angle X-ray diffraction (HA-XRD), low angle X-ray diffraction (LA-XRD). HfN and VN layers were analyzed by X-ray photoelectron spectroscopy (XPS) and electron and transmission microscopy (TEM). HA-XRD results showed preferential growth in the face-centered cubic (111) crystal structure for HfN/VN multilayer systems with the epitaxial relation (111) $[100]_{HfN}$//(200) $[100]_{VN}$. The maximum coherent assembly was observed with presence of satellite peaks. With this idea, ternary and binary nitrides films have been designed and deposited on Si (100) substrates with bilayer periods (Λ) in a broad range, from nanometers to micrometers. The films were fabricated to study the structural evolution, coherent assembly progress and optical properties such as the critical angle, dispersion coefficient, index of refraction for HfN/VN multilayers with decreasing bilayer thickness.

Introduction

Binary materials, like TiN and CrN, have received considerable attention as wear-resistant coatings because of their high mechanical hardness, wear resistance, and chemical inertness. However, the mechanical requirements in many applications are so high that classical single-layered hard coatings cannot satisfy them anymore [1]. Several films such multilayer materials have attracted much research interest because the nanometer scale may drastically change the density of electronic states and the transport properties of the conductor or semiconductors systems [2]. In the literature is presented that strain-driven self-assembly of nanostructures provides an inexpensive and effective manufacturing process and has been extensively studied over the past decade. Tuning the size distribution and spatial ordering of these structures remains a continuing challenge. Metal/metal, metal/ceramic and ceramic/ceramic are type of the model materials used in the investigation of the self-organization of nanostructures in semiconductor and mechanical heterostructures [3–5]. In the case of iso-structural multilayers (e.g., NaClfcc–NaClfcc), molecular dynamics (MD) simulations have shown that the peak strength is set by coherency stresses which in turn are determined by elastic modulus and lattice parameter mismatch [6]. Thus, heterostructures systems such as CrN/ZrN [7] composed by metal/ceramic and ceramic/ceramic superlattices combination have received much attention because these combinations can exhibit high hardness values, often increasing by more than 100% over the rule-of-mixture values, while retaining good physical properties. In this sense, the literature presents few researches focused on studying the effect of the transition-metal-nitride superlattice. Such effect on ceramic substrates coated with TiN/NbN, TiN/VN, NbN/VN has been study and reported by Sproul [8]. In that study, the authors found that polycrystalline superlattice films have hardnesses above 50 GPa, when the superlattice period is in the range of 4–8 nm, and this hardness enhancement depends strongly on control of the process parameters [8–10]. Taking into account the above, the synergy between superlattice effect and its physical properties on silicon substrate coated with HfN/VN has not yet been thoroughly studied. In this work, the HfN/VN multilayers coatings with total thickness of ~2.4 μm have been designed and deposited on Si (100) substrates with bilayer periods in a broad range, from few nanometers to several nanometers, with the aim to study the structural evolution with decreasing bilayer thickness (Λ) and their relationship to coherent assembly as function of the correlation length. Potential technological applications could be in the electronic and optical industries.

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Experimental details

Multilayers 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 used for all substrates under argon atmosphere. Two metallic Hf and V targets with 10 cm of diameter and purity at 99.9% for both targets were used. A 350 W magnetron power was applied to the hafnium target, while a power of 400 W was applied to the vanadium target. Substrate–target distance of 7 cm, substrate temperature of 300 °C; under circular rotation substrate with 60 RPM to facilitate the formation of the stoichiometric binary coatings, which is necessary for obtaining the face centered cubic (FCC) crystal structure. The substrate for this work is a square-shaped structure with an area of 1 cm^2. The mixture of (80%) for Ar gas and (20%) for N_2 gas was introduced into the chamber with a total working pressure of 6×10^{-3} mbar. An unbalanced r.f. bias voltage was applied, which generates a negative signal fixed at −50 V. Moreover, it was possible to vary the bilayer number ranging from 1, 10, 30, 50, 80 and 200. Therefore, these multilayer values changed the bilayer period due to the increase of the bilayer number for coatings with constant thickness. The X-ray diffraction (XRD) study was carried out for a multilayer systems in high-angle ranges and low-angle ranges with a Bragg–Brentano configuration ($\theta/2\theta$), where the crystal was analyzed by using a Philips-MRD diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å). The chemical composition was analyzed via X-ray spectroscopy photoelectron (XPS). XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X ray source (Aluminum Kα line of 1486.6 eV energy and a power applied of 300 W and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 1.1 eV. The selected resolution for the spectra was 30 eV of Pass Energy and 0.5 eV/step for the general survey spectra and 10 eV of Pass Energy and 0.15 eV/step for the detailed spectra of the different elements. All Measurements were made in an ultra-high vacuum (UHV) chamber at a pressure around 5×10^{-8} mbar. Samples were etched for 5 min with an Ar^+ ion beam with energy of 3 keV. Moreover, C 1s spectra were fitted with software CasaXPS V2.3.15 using Gaussian Lorentzian functions (after a Shirley background correction) where the FWHM of all the peaks were constrained while the peak positions and areas were set free. Low-angle (LA-XRD) or reflectivity (XRR) scans permitted the characterization of the preferred-orientations related to epitaxial growth. Bilayer periods in multilayers were measured using low-angle XRD ($\theta/2\theta$) scans and compared with those obtained from transmission electron microscopy (TEM) micrographs. The structural assembly of the multilayer coatings was analyzed by TEM using a Philips CM30 microscope operating at 300 kV and by simulations of low-angle XRD patterns using Paratt's formalism [11].

Results and discussion

HA-X-ray analyses for multilayers coatings

The measured total thickness for $[HfN/VN]_n$ multilayers was found to be approximately 2.4 μm for all of them. The individual thickness varied in function of bilayers number from $n = 1$ to $n = 80$ producing layers with thicknesses from 1.2 μm to 15 nm, respectively. Fig. 1 shows the high-angle X-ray diffraction patterns corresponding to the HfN/VN multilayers. There is a clear evolution of diffraction patterns in this set of multilayers as the bilayer period is reduced. As seen in Fig. 1a, at large bilayer periods, there is a clear FCC (111) preferred orientation for both Hf–N and V–N layers [12]. The VN layers texture remain constant the (111) preferred orientation present from 1.2 μm-thick films to multilayers with 15 nm-thick; this behavior suggests the possibility of a cube-on-cube epitaxial growth. In the thickest bilayer pattern there are still some small contributions of VN (200), HfN (311) and HfN (222) reflections, but they disappear for a large range of bilayer periods till the thinnest multilayer period $\Lambda \leqslant 15$ nm.

The VN (111) peak position suffers a great deviation from the bulk value indicating a possible stress evolution of HfN/VN layers with the bilayer period. The quasi-relaxed position observed for thinner bilayer periods was progressively shifted to higher compressive stress values as the bilayer period is increased until the $\Lambda = 1.5$ μm value is reached. For thinner period multilayers ($n = 80$), an abrupt change in V–N (111) peak position was observed, presenting a stress reduction due to the movement of this peak toward higher angles compared to other multilayers but close to bulk value (34.24°). The stress evolution showed for (111) peak position into the XRD patterns (Fig. 1a) is accompanied by a progressive and intense symmetrical enlargement according to the increase of intensity peak. Moreover, these patterns show clearly that the widening peaks are reduced accordingly with the decrease of bilayer number and increase in the thickness of individual layers [10,13]. Moreover in the Fig. 1b it was possible to observe the reduction in the intensity of Hf–N (311) and Hf–N (222) signals when the bilayer numbers are reduced, possibly associated to increase of multilayer stress.

Maximum peak shift and crystallographic structure simulations

For a large bilayer period, there is a clear face centered cubic (FCC) (111) preferred orientation for HfN layer and FCC (200) preferred orientation for V–N layers (isostructured multilayer) Fig. 2a. These preferential orientations agree with JCPDF-00 033 0592 (HfN) and JCPDF-00 035 0768 (VN) from ICCD cards. The texture of HfN layer remains constant in preferential orientation (111) from 1200 nm thick films to multilayers with 15-nm thickness. So, from the individual patterns for HfN and VN coatings it was possible to observe a difference in the peak positions for (111) direction, which indicates a difference of lattice constant. Thus, suggesting that the peak preferential direction (111) for the multilayer is a possible combination between HfN and VN peaks. Then, the more intense (111) peak can be one solution of the combination between them. The satellite peaks were observed for multilayer samples as function of bilayer period (Λ) Fig. 2a. It is clearly shown that relative intensity for highest intense peak is referred to the central peak which is associated even cube-on-cube assembly, this cube-on-cube behavior is affected by increase of bilayer period where the great lattice disorder is due to residual stress between HfN and VN layers. Other possible reason can be decreasing amount of crystallites which built the cube-on-cube assembly when the layer thickness is increased.

On the other hand, the quasi-relaxed position observed for thinner bilayer periods was progressively shifted to higher compressive stress values as the bilayer period increased up to the $\Lambda = 1200$ nm value. Thus, the crystallographic structure simulations for HfN and VN (Fig. 2b), confirm the coherent ensemble with a mismatch of 8.11%. Finally, for thinner multilayered periods ($n = 80$, $\Lambda = 15$ nm), a continuous transition of Hf–N (111) peak position was observed, from multilayers coatings with bilayer periods of 120 nm to those with 15 nm bilayer period in agreement with crystal simulation for cube-on-cube assembly taking into account the HfN/VN mismatch with the epitaxial relation for HfN/VN from out-plane information (XRD results) HfN (111), and VN (200).

Satellite peaks and superlattice effect

The existence of maximum peaks present in all periods from $\Lambda = 1.2$ μm to $\Lambda = 15$ nm (Fig. 3), is associated with the short