Determination of superlattice effect on metal–ceramic nano-structures

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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 (l) 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 (l) 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.

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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 (l) and their relationship to coherent assembly as function of the correlation length. Potential technological applications could be in the electronic and optical industries.
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 at 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 cm². The mixture of (80%) for Ar gas and (20%) for N₂ gas was introduced into the chamber with a total working pressure of 6 × 10⁻⁵ 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 (θ/2θ), where the crystal was analyzed by using a Philips-MRD diffractometer with Cu-Kα radiation (λ = 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 (θ/2θ) 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 [111].

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 (1 1 1) preferred orientation for both Hf–N and V–N layers [12]. The VN layers texture remain constant the (1 1 1) 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 (2 0 0), HfN (3 1 1) and HfN (2 2 2) reflections, but they disappear for a large range of bilayer periods till the thinnest multilayer period A ≤ 15 nm.

The VN (1 1 1) 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 A = 1.5 μm value is reached. For thinner period multilayers (n = 80), an abrupt change in V–N (1 1 1) 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 (1 1 1) 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 (3 1 1) and Hf–N (2 2 2) 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) (1 1 1) 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 (1 1 1) 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 (1 1 1) direction, which indicates a difference of lattice constant. Thus, suggesting that the peak preferential direction (1 1 1) for the multilayer is a possible combination between HfN and VN peaks. Then, the more intense (1 1 1) peak can be one solution of the combination between them. The satellite peaks were observed for multilayer samples as function of bilayer period (A) 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 A = 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, A = 15 nm), a continuous transition of HF–N (1 1 1) 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 HN/VN mismatch with the epitaxial relation for HfN/VN from out-plane information (XRD results) HfN (1 1 1), and VN (200).

Satellite peaks and superlattice effect

The existence of maximum peaks present in all periods from A = 1.2 μm to A = 15 nm (Fig. 3), is associated with the short
spacing red connection out-of-plane between HfN (111) and VN (200) layers: (aHfN (111)/aVN (200) = 1.0883). As indicated in similar cases by other authors [10], solving an envelope function with two central maximum, which converges to a single maximum value that occurs over relatively small periods (around or below 15 nm). This can be observed for the combinations of two materials (HfN and VN) with a short spacing relation red (red parameter) out-of-plane as observed in this research for metallic nitride multilayers with bilayer periods between \( K = 80 \text{ nm} \) and \( K = 15 \text{ nm} \). Thus, it is possible to analyze a high central peak which is derived from the modulation of both metal nitride materials and nanometer multilayer characteristics. Therefore, the analysis of these satellites superlattice peaks can be related to the case of a coherent set of stacking layers associated with HfN and VN with presence to the wide range of bilayers that involves a large structural coherence length \( (\xi) \) along the growth direction. For the case in which the length \( (\xi) \) is very different (shorter) than the modulation period \( (\Lambda) \), it is possible to generate a XDX signal without satellites peaks diffractions Fig. 3a. This behavior is attributed to periods usually very large or a very disorderly structure (amorphous) of one of the constituent materials [14–16].

Nevertheless, Yashar and colleagues [10] presented another possibility which agrees with results shown in this paper, when the multilayer period is higher than \( K \geq 60 \text{ nm} \). So, the explanation of this disappearance of superlattice peaks in XRD results, for similar multilayers is related to the internal disorder of the
material and residual stresses, both associated with a large red mismatch between the materials, and the resulting interfacial roughness. Moreover, it is possible to observe a tendency manifested in the increased stress (residual stress) for HfN/VN multilayers coatings when reducing the bilayer number (ie, \(n = 1\) and \(n = 30\)), which can also be deduced that the large shift suffers peak position in HfN/VN (111) up to period values below 15 nm.

However, the metal-nitride multilayer systems can theoretically provide a low mismatch around 1.08% between the coupling of the red parameters that present each of the individual layers, which are constituents in the multilayer systems \(\Lambda = 15\) nm. Thus, during intermediate and low bilayer periods, there are some modulations of symmetrical diffraction intensity. However, the HA-X-ray patterns are taken generally in high geometry (\(\theta/2\theta\)), wherein the scattering vector, \(|\mathbf{q}| = 4\pi\sin(\theta)/\lambda\), and is perpendicular to the multilayer interfaces. So, the HA-X-ray patterns may consist of a convolution of the grid spacing variation and the compositional modulation. Due to this condition, the high angle diffraction patterns are more difficult to interpret than the patterns of X-ray diffraction of a low angle [10,15]. The peaks shown in (HA-XRD), also contain detailed information about red spacing variation. Therefore, when red spacing out-of-plane of the individual layers are similar (\(n = 80\) or \(\Lambda = 15\) nm with mismatch of 1.08%), the pattern generally consists of a Bragg peak located at half the spacing red between the HfN/VN multilayer surrounded by equidistant satellites peaks (in reciprocal space) Fig. 3a. Moreover, it is possible to observe the Curling patterns (Fig. 3b) after subtracting the satellites peaks (in reciprocal space) Fig. 3a. Moreover, it is possible to observe the Curling patterns (Fig. 3b) after subtracting the satellites peaks (in reciprocal space). Consequently, it is possible to observe that, nitrogen content in HfN and VN films acts as a dopant.

Taking into account the above discussion, the satellite peak intensities refer to the magnitude of the composition modulation (Curling patterns Fig. 3b). That is, the relationship between the intensity peaks of the satellite order (m-th) and the intensity of the Bragg peak, \(I_{\text{Br}}/I_{\text{B}}\) component is related to the Fourier compositional modulation (m-th). Therefore, if the HfN/VN multilayers do not have a perfect square wave representing the modulation compositional, the satellite peak intensities decrease with higher order peaks that are generally more affected than lower order peaks [16].

Fig. 4 shows that (\(n = 80\), \(\Lambda = 15\) nm) layers were grown with high orientation in relation to the substrate, and with high intensity of the Bragg peak. Thus, even for small ratios \(I_{\text{sat}}/I_{\text{B}}\) the satellite peaks are observed [10]. The satellite peak positions are associated with a maximum corresponding to a respective local order (m). Therefore, it can be applied to the second derivative from Curling patterns (Fig. 3b), and thus find the local maximum to zero (Fig. 4a). Moreover, \(\sin(\theta)\) as function of satellite peak order can be analyzed with linear behavior satellite peak positions \((\theta_{\pm})\) and the reflection order \((\lambda)\) associated with each local maximum, shown in Fig. 4b, revealing good definition of the multilayers and uniform periodicity [17].

**Chemical composition via XPS analysis**

XPS survey spectra for HfN and VN single layers that make up the HfN/VN multilayers coatings deposited with \(n = 1\) (\(\Lambda = 600\) nm) are shown in Fig. 5. According to XPS literature, regarding Hf–N and V–N coatings materials [18,19], concentration measurements and identification of the specific bonding configurations for the HfN and VN layers are more reliable when XPS analysis is used. So, the core electronic spectra carry information of the chemical composition and bonding characteristics of the HfN and VN coatings generate an increase in the reliability of the results. Finally, the nitrogen (N) signal presence can be associated to a few surface contaminations. In this sense, binding energies’ identification was realized in agreement with NIST X-ray photoelectron spectroscopy Database 20, Version 3.5. So, the integral N1s, Hf4f and V2p3/2, spectra corrected by relevant sensitive factors can evaluate the concentrations of N and Hf elements for Hf–N coatings and N, and V elements in the V–N coating. The corresponding integral of the deconvoluted peaks can also be used to estimate the bond contents, which are described by the following Eq. (1) [20]:

\[
C_i = \frac{\sum (I_i)}{\sum (I_i)}
\]

where \(S\) is the sensitivity factor, \(A\) is the integral of deconvoluted peaks, and \(C_i\) is the atomic content. The numerator is the sum of the integral of one sort of bond; the denominator is the sum of the integral of all types of bonds decomposed from the whole peak of N1s, Hf4f and V2p3/2, spectra in the sample. Table 1 shows that there is prevalence of nitrogen and hafnium atoms, for Hf–N material and nitrogen and vanadium atoms, for V–N material, which means majority presence of nitride phases such as is showed in the X-ray diffraction Pattern (Fig. 1). In this sense, binding energies’ identification was realized in agreement with NIST X-ray photoelectron spectroscopy Database 20, Version 3.5. So, the core electronic spectra carry information of the chemical composition and bonding characteristics of the HfN and VN layers are more reliable when XPS analysis is used. So, the core electronic spectra carry information of the chemical composition and bonding characteristics of the HfN and VN coatings.
Fig. 6b shows energy bindings for Hf–O–N (17.2 eV) and Hf–O (14.3 eV). The change of binding energy compared to HfN single layer materials verifies the formation of Hf–N layer; therefore, calculating the peak area yields an atomic ratio of Hf:N = 0.1:0.9, similar to the stoichiometry of Hf$_{0.1}$N$_{0.9}$ [18].

On the other hand, for VN material (Fig. 7) the peaks with highest intensity correspond to N–V (397.4 eV) at N1s signal and V–N (514.6 eV) at V2p3/2 signal. In this sense, for N1s signal (Fig. 7a), the energy bindings for N–V–O (402.0 eV) and N–O (400.0 eV) were found. Moreover, Fig. 7b shows energy bindings for V–O (516.8 eV). The change of binding energy compared to VN verifies the formation of binary V–N compound; therefore, calculating the peak area yields an atomic ratio of V:N = 0.2:0.8, similar to the stoichiometry of V$_{0.2}$N$_{0.8}$ [19].

**Low-angle X-ray diffraction (XRR) analysis**

The real nanometric features of HfN/VN multilayers coatings, X-ray reflectivity analysis (XRR), otherwise called low-angle X-ray diffraction (LA-XRD), were employed to obtain precise measurements of bilayer periodicities and also to give some indication of the combined effect of interfacial roughness and intermixing. LA-XRD data, such as the plotted in the Fig. 8a, were obtained for most of the HfN/VN systems confirming a well-defined and stable multilayer periodicity at the nanometric scale which was observed from HA-XRD results (Figs. 1 and 2). Thus, the bilayer periodicities can be extracted directly from the peak positions. Simulations were also performed to fit the experimental data using Paratt’s formalism [11]. From LA-XRD results, it was directly possible to obtain the thickness ratios; but neither interface roughness nor diffuse widths, can be extracted independently, only a combined value of both, as it cannot discern between those two effects (thickness ratios and interface roughness) [8,21,22].

Moreover, Fig. 8a presents X-ray reflectivity peaks exhibiting low intensity and are quickly lost into the noise region for relatively small angles. The reduced intensity of peaks shown in this analysis has its main origin in the very low difference in electron density between both, HfN and VN binary materials. This physical property (electron density) causes the modulation on X-ray reflectivity signal for the current multilayer systems due to dissimilar materials. Otherwise, the fast drop of reflectivity signal for low angles can be related to different microstructural defects such as roughness, intermixing, different chemical nature observed by XPS results (Fig. 5) and other interfacial distortion effects that produce dispersion of X-ray intensity, instead of reflection [23].

On the other hand, taking into account the XRR results (Fig. 8a), Fig. 8b shows Sin$^2$(θ) as a function of the maximum order of intensity. From this figure, it is clearly seen a linear behavior relating to the increase in the order of maximum and θ increases, adjusting thus, various results of reflectivity similar to those used in this

**Table 1**

Chemical composition of Hf–N and V–N coatings from XPS results.

| Chemical composition | N (%) | Hf (%) | V (%) |
|----------------------|-------|--------|-------|
| Hf–N coating         | 0.9   | 0.1    | –     |
| V–N coating          | 0.8   | –      | 0.2   |

Fig. 5. XPS survey spectrum: (a) HfN coatings and (b) VN coatings deposited on Si with an r.f. negative bias voltage of –30 V.

Fig. 6. High-resolution spectrum for HfN coatings: (a) N1s, (b) Hf4f signals.
The scientific literature shows that several authors have postulated an attempt to describe some models for such linear behaviors. For instance, Paratt and Yashar have worked on a linear model that considers the period, the modulation order, and the scattering coefficient among other features present in many multilayers, generating an equation that assumes different phenomena in the reflectivity (XRR), which is widely accepted [6, 10, 24, 25]. So, the multilayer period ($K$) can be determined from the following Eq. (2):

$$\sin^2(\theta) = \left(\frac{\lambda}{2L}\right)m^2 + 2\delta$$

where $\theta$ is the angle between the X-ray and the scattered planes, $\lambda$ is the wavelength of X-ray (1.5406 Å), $L$ is the bilayer period, $m$ corresponding to the maximum order of intensity, and $\delta$ is the scattering coefficient of the multilayer. From Eq. (2) for HfN/VN multilayers it was determined a theoretical period of $n = 30$, thus the value found for $K_T$ was 40.3 ± 0.5 nm, which broadly corresponds to the nominal value $K_T = 40$ nm.

From Fig. 8, another remarkable feature can be disclosed when comparing the experimental and the simulated spectra. This is the evident broadening of the experimental peaks which can be correlated to their lower intensity when compared to those of the simulations, as in this way the peak area integral is maintained quite similar in all cases. This effect can be directly related to some amount of spreading on bilayer period values through the whole coating thickness and/or the radial distance. Bilayer periodicity ($A$) sets the precise position of X-ray reflectivity maxima, as in the simulated spectra. And so, a slight variation on the periodicity causes an intermixing of the reflectivity signals originated at different compositional modulations that, on the one hand, produces peak broadening, inducing thus an additional reduction of peak intensity [21]. This spreading can only be properly measured for peaks at high angles, such as the second maxima of the multilayer with $A$ lower than $A = 5$ nm, where the variation on periodicity is $\Delta A = 0.2$ nm. In the other multilayer or superlattice this spreading effect can only be hinted but is not clear enough to be measured [26]. To summarize, all the relevant values extracted from LA-XRD data and simulations have been put together in Table 2, thus, it can be observed that all the bilayer periods measured from reflectivity coincide quite closely with those already calculated from theoretical models.
Transmission electron microscopy (TEM) analysis

TEM results presented in Fig. 9 allow a detailed examination of the microstructural details such as growth patterns, the periodicity of the HfN/VN multilayers and a study of the interfaces. In the TEM results the darker contrast corresponds to the binary layer (Hf–N) in relation to the other binary (V–N) layer associate to deferent chemical composition observed in XPS results (Fig. 5), in this sense TEM results allows a clear determination of the structure and interfaces between the layers. Therefore, Fig. 9 shows a typical TEM bright field image for HfN/VN system, which evidences the multilayer structure, showing diffraction patterns for both layers with their orientation preferential HfN (1 1 1) and VN (2 0 0). Thus, the TEM image (Fig. 9) clearly reflects the existence of a stable layer structure and periodic layer with moderate modulations in the nanometric range. Also TEM images show alternating layers of HfN (thin) and VN layers (thick). Moreover, the alternating layers are in structural coherency with the satellite peaks presented in (Figs. 2 and 3). In this regard, the last effect generated by the alternating HfN and VN layers coinciding with the LA-XRD (XRR) results and XRR simulations (Fig. 8).

However, the complete structural information can be extracted by the selected area electron diffraction patterns (SAED), as presented in Fig. 9 (insert). These SAED patterns are representative of the diffraction patterns obtained from the selected regions within HfN/VN multilayers, therefore, these patterns clearly show different crystalline structures with strong preferential growth in the HfN (1 1 1) and (2 0 0) for VN layer associated with both materials composing the multilayers coatings [27]. Finally, the TEM images show, in terms of the interplanar distance, that HfN layer (d = 0.2612 nm) is marginally lower than VN layer (d = 0.2063 nm). They also confirmed that for the interplanar distance in HfN and VN layer there is a deviation of 0.0549 nm. Therefore, it was possible to determinate the epitaxial relation for HfN/VN system from out-plane information (XRD results Fig. 1) HfN (1 1 1), VN (2 0 0) and in-plane information (TEM results Fig. 9) HfN [1 0 0], VN [1 0 0] (1 1 1) [1 0 0][HfN/(2 0 0)] [1 0 0][VN].

Critical angle, dispersion coefficient and index of refraction

In Fig. 10 the LA-XRD (XRR) results for the HfN/VN multilayer systems deposited with n = 30 are shown. In these results (Fig. 10a), the first two changes in reflectivity signal associated to the critical angles for Si (1 0 0) (ΘcSi(100)) and HfN/VN (ΘcHfN/VN) materials are observed. Since changes in the XRR signal for the Si (1 0 0) and the HfN/VN system are hardly observable and considering that XRR problems can be seen as an XRD problem of a one unit cell film of a material with the out-of-plane parameter equal to the thickness of the sample, therefore in the Fig. 10b it was necessary to determine the true critical angle deriving the signal reflectivity in relation to (θ) angle like (dR/dθ) [11,21,28].

On the other hand, from the true critical angle results for the multilayer HfN/VN system (Figs. 8–10), it was determined that the critical angle (Θc) is related to its average electronic density (ρe) described by Eq. (3) [11,28].

\[ \Theta_{cHfN/VN} = \sqrt{\rho_e r_e^2 / \pi} \] 

where \( \Theta_c \) is the critical angle, \( \rho_e \) is the electronic density, \( r_e \) is the electron radius (2.817950 x 10^{-15} m), \( \lambda \) is the wavelength of X-ray (1.5406 Å). Analyzing the last expression, from Eq. (3) for HfN/VN multilayers, a theoretical electronic density \( \rho_e(HfN/VN) = 2.688 \times 10^{23} \text{el/m}^3 \) was determined.

Taking into account the last results, it was possible to determine, by using Snell’s law and Paratt’s formalism [11], the \( \delta \) = dispersion coefficient and index of refraction for HfN/VN multilayer associate to the next Eqs. (4) and (5).

\[ \delta = \left( \frac{1}{2} \cdot \pi \right) \cdot r_e \cdot \lambda^2 \cdot \rho_e \]
where $\delta = \text{dispersion coefficient}$, $r_e$ is the electron radius 
$(2.817950 \times 10^{-13} \text{ m})$, $\lambda$ is the wavelength of X-ray (1.5406 Å), $\rho_e$ is the electronic density. From Eq. (3) for HfN/VN multilayers the dispersion coefficient $\delta_{\text{HfN/VN}} = 0.28424$ el was determined. Furthermore, the refractive index $(n)$ of the materials is smaller than unity in the hard X-ray region. This is a consequence of the repeated resonant behavior of many possible electronic transitions up to the X-ray region. Thus, the index of refraction for HfN/VN was determined by Eq. (4) [11,28]:

$$n = 1 - \delta - i\beta \quad \text{if} \quad \text{Re}(n) < 1 \Rightarrow n \approx 1 - \delta$$

(5)

where $n$ is the index of refraction, $\delta$ is the dispersion coefficient, and $\beta$ is the absorption coefficient. However, the two real numbers $\delta$ and $\beta$, have dependencies of HfN/VN material and wave-length dependencies taking into account that $\delta$ is a reduction due to the binding of the electrons in the atom, which is proportional to the electron density $(\rho_e)$ of the material and inversely proportional with the square of the wavevector $k$. The imaginary part is related to the absorption of X-rays, $\beta$ being proportional with the absorption coefficient. In this regard, from Eq. (4) for HfN/VN multilayers, an index of refraction $n_{\text{HfN/VN}} = 0.7157$ was determined.

**Conclusion**

X-ray diffraction results obtained by HfN/VN multilayers showed at low and high angles evidencing compositional superlattice reflections. The textured multilayer grew with the (111) direction perpendicular to the substrate surface and a relationship $\theta_{\text{HfN}(111)}/\theta_{\text{VN}(200)} = 1.0883$. The peak characteristics of a superlattice satellites were detected for the binary multilayer systems with $n$ between $n = 30$ and $n = 80$ or bilayers periods between $A = 40$ nm and $A = 14$ nm.

The chemical composition via XPS results showed that the Hf$_{1.0}$N$_{0.9}$ and V$_{2.0}$N$_{0.8}$ layers preserve acceptable stoichiometry for binary metal nitride synthesized with transition metal, moreover, from the structural analysis by SAED and HR-TEM it was observed with high precision that HfN and VN materials within multilayer systems possess the same crystal structure (FCC) with similar tendencies taking into account that $\delta$ is the absorption coefficient. However, the two real numbers $\delta$ and $\beta$, have dependencies of HfN/VN material and wave-length dependencies taking into account that $\delta$ is a reduction due to the binding of the electrons in the atom, which is proportional to the electron density $(\rho_e)$ of the material and inversely proportional with the square of the wavevector $k$. The imaginary part is related to the absorption of X-rays, $\beta$ being proportional with the absorption coefficient. In this regard, from Eq. (4) for HfN/VN multilayers, an index of refraction $n_{\text{HfN/VN}} = 0.7157$ was determined.

**References**

[1] Chen YH, Lee KW, Chouaia CH, Chung YW, Keer LM. Synthesis and structure of Escobar CA, Caicedo JC, Aperador W. Corrosion resistant surface for vanadium Yashar Philip C, Sproul William D. Nanometer scale multilayered hardcoatings. [2] Paratt LG. Surface studies of solids by total reflection of X-rays. Phys Rev A. Chaudhuri J, Alyan SM, Jankowski AF. Analysis of Ni/Ti multilayers by X-ray Fewster Paul F. X-ray analysis of thin films and multilayers. Rep Prog Phys. Tari S. An interface study of crystalline Fe/Ge multilayers grown by molecular Glaser A, Surnev S, Ramsey MG, Lazar P, Redinger J, Podloucky R, Netzer FP. The Zhou Y, Ogawa M, Bao M, Han W, Kawakami RK, Wang KL. Engineering of Tari S. An interface study of crystalline Fe/Ge multilayers grown by molecular Glaser A, Surnev S, Ramsey MG, Lazar P, Redinger J, Podloucky R, Netzer FP. The fewster paul f. x-ray analysis of thin films and multilayers. rep prog phys. tari s. an interface study of crystalline fe/ge multilayers grown by molecular  

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![Fig. 10. Reflectivity (XRR) signal for HfN/VN system. (a) different critical angles for Si (100) substrate and (b) HfN/VN multilayers associate to derive LA-XRD signal dR/dd].
[20] Zhuang C, Zhao J, Jia F, Guan C, Wu Z, Bai Y, Jiang X. Tuning bond contents in B-C-N films via temperature and bias voltage within RF magnetron sputtering. Surf Coat Technol 2009;204:713.

[21] Blaurock AE, Worthington CR. Treatment of low angle X-ray data from planar and concentric multilayered structures. Biophys J 1966;6:305–12.

[22] Yasaka Miho. X-ray thin-film measurement techniques. Rigaku J 2010;26(2):1–9.

[23] Suzuki T, Omote K, Ito Y, Hirosawa I, Nakata Y, Sugiura I, Shimizu N, Nakamura T. Thin Solid Films 2006;515:2410–4.

[24] Kurokawa A, Odaka K, Fujimoto T, Azuma Y. Shinku J Vac Soc Jpn. 2007;50:199–201.

[25] Stearns DG. J Appl Phys 1989;65:491.

[26] Bagchi S, Singh F, Avasthi DK, Lalla NP. J Phys D Appl Phys 2009;42:145414.

[27] Haihua L, Nini P, Jørgen S, Xiaoxu H. Quantitative TEM analysis of Al/Cu multilayer systems prepared by pulsed laser deposition. J Appl Phys A 2010;101:677–80.

[28] Gu YS. Structural studies of Fe/Pd magnetic multilayers by X-ray diffraction. Phys Rev B 1994;50:6119.