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XPS, AES, and EELS characterization of nitrogen-containing thin films

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Abstract

Pulsed laser deposition (PLD) appears to be a very efficient tool for material synthesis. Interstitial compounds like hydrides, carbides, and nitrides are usually produced by reactive variations of PLD. In this study, a methodical routine based in PLD is used to synthesize nitrogen-containing films by ablating pure-element targets in molecular nitrogen environments. The resulting films are analyzed in situ by X-ray photoelectron (XP), Auger-electron (AE), and electron energy loss (EEL) spectroscopies. Our methodology confirms the existence of remarkable regularities in the spectroscopic characteristics of those films. For example, the N-KVV Auger transition for nitrogen contained in d-metals is split in three main energy bands and several additional subbands. For the main bands, their relative intensities correlate with electronic populations in d-orbitals, while the subbands can be associated to energy losses of the main bands. We propose that the main bands reflect the bonding, non-bonding and anti-bonding interactions between nitrogen and partner element. By means of XPS measurements, core-level energy shifts are detected and they are relative to the amount of nitrogen incorporated in the films. In the EELS section, an association between the loss-structure of pure-elements and nitrides is presented. With few exceptions, the bulk plasmon energy in nitrides is larger than in pure-elements, indicative of an increase in the electronic density of nitrides. The peak structure of the N-KVV transition, the XP binding energies and the loss spectra are presented; this data can be of valuable assistance for the analysis of nitride formation.

Keywords: AES; EELS; XPS; Nitrides; AES peak structure; PLD

1. Introduction

Nitrides constitute a class of materials with many technological applications. Mainly, the attention is set in refractory nitrides because of their great strength and durability that permit their use at extreme conditions [1]. Their exceptional combination of properties, like hardness, chemical inertness, electrical conductivity, and optical properties have allowed them to be used for applications in cutting tools, in diffusion barriers, in electrical contacts, in less-coatings, etc. However, not all nitrides develop stable materials. Some of the unstable nitrides can have applications in situations where that property is conveniently used. For example, copper nitride (Cu_3N) can be used as a precursor material for microscopic electrical contact lines by maskless laser writing [2,3] and platinum nitride, to produce highly oriented platinum electrodes [4].

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For simplicity, the nitride forming element will be called Me, even if some are not metals. In general, nitrides are considered interstitial compounds due to the tendency of the N atoms to lie in the interstices of the closed-packed Me-lattice [5]. Currently, the chemical environment of interstitial compounds is the subject of much speculation. It is likely that improvements in utilization of these compounds will occur by the understanding of the interstitial-atom role in the electronic band-structure of the receiver-lattice [6]. This will lead to the discovery of new phases or alloys with singular properties. Certainly, to progress in that direction, comprehensive characterizations are mandatory. However, very little work is available with in situ spectroscopic characterization of the as-produced nitride thin films. As a consequence, samples were either analyzed under various degrees of surface contamination of adventitious C and O, or this contamination was removed by sputtering with energetic Ar ions, with the possibility of considerable sample damage and subsequent uncontrollable reduction.

In this work, we intend to provide spectroscopic data of in situ analyzed nitrogen-containing thin films. With this aim, a

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large set of thin films were synthesized by pulsed laser deposition (PLD) of metallic targets in N_2 environments, and in situ analyzed by X-ray photoelectron (XP), Auger-electron (AE), and electron energy loss (EEL) spectroscopies. The results are categorized in terms of the spectroscopic regularities and discrepancies that they present. We will show that the spectroscopic characteristics in our films are representative of some chemical states that can be found in nitrides.

2. Synthesis of nitrides by PLD

It is possible to stabilize metastable materials that cannot be synthesized in bulk by growing thin films with an appropriate choice of deposition techniques and conditions. Due to the energetic laser-target-ambient interactions, PLD is capable of depositing metastable materials that are difficult to synthesize in bulk or by other deposition methods. So, it represents an attractive and efficient method for material synthesis. One of the most widespread modifications to the basic PLD approach involves the addition of a background gas during the deposition process [7]. The background gas helps in moderating the energy of ablated species, achieving an important decrease in the concentration of ejected ions from the target that are transmitted to the substrate. Moreover, the interactions of the plume with the reactive environment (which happen not only in the gas phase but also on the target and substrate surface) play an important role in producing the atomic and molecular precursors required for the growth of the compound phase. The resultant stoichiometry is closely associated and controlled by the pressure of the background gas [8]. This reactive variety of PLD, now called RPLD, has been exploited successfully to produce several oxides, nitrides, carbides, and silicides. The method is seen to provide an adequate tool for tuning the amount of nitrogen incorporated in the films. Numerous parametric studies have been carried out to achieve a fine control of composition and the structure of the deposited films, but the exact formation process of compounds by the RPLD method has not been fully understood. This is due to many problems encountered in the precise characterization of deposited films. The topic of nitride processing by RPLD was recently reviewed by Perrone [8]. Previous studies by our group [9–17] aimed to produce binary nitrides by means of RPLD, showed a nitrogen saturation pressure, $P_{\rm S}$, for which the nitrogen incorporation in the films reaches a maximum value. We found that this $P_{\rm S}$ depends, mainly, on the nitrogen affinity of the ablated material. Additionally, it has small dependencies on other parameters, like target-surface conditions, laser energy, and pulse repetition rate. For instance, according to the conditions given in Section 3, P_S is 1 mTorr (1 mTorr = 0.13 Pa) for yttrium [15]; while for copper is near 100 mTorr [16]. These two examples show favorable and unfavorable Me-N reactions.

3. Experimental

3.1. Sample preparation

This work is based in a very simple experiment: it consists in laser ablating pure-element targets in vacuum and in N_2 environment. In the initial stage, a pure-element film is deposited in the growth chamber over a silicon wafer at ultra high vacuum (UHV) conditions. After that, the sample is transferred to the adjacent analysis chamber for XPS, EELS, and AES data acquisitions. Next, the same sample is carried back to the growth chamber. A new layer is deposited on top of the metallic film, in this instance at certain nitrogen pressures, P_N , growing a two layer-system. Again, the film is characterized by the available spectroscopies.

All depositions are carried out in a modified laser ablation system, Riber LDM-32. A complete description is in [7]. In brief, the system consists of three chambers: sample loading, film growth, and analysis. Each chamber is isolated by gate valves and independently evacuated by ion pumps. The analysis chamber is equipped with an electron-energy analyzer model Mac-3, an e-gun and a dual anode X-ray source, all from Cameca. This configuration enables us to make in situ XPS, AES, and EELS analyses.

All depositions were accomplished by ablating high purity targets, \sim 99.9 wt.%, commercially available from Alfa-Aesar. The films were grown on silicon wafers. Before the actual deposition process is started, the system is evacuated to a base pressure in the 10^{-10} Torr range for the growth and analysis chambers, and in the 10^{-9} Torr range for the introduction chamber. For the pure-element films, depositions are performed in UHV conditions, achieving carbon-free films and oxygen concentration less than 4 at.% for the most reactive metals. For nitrogen-containing films, a N₂ flow in the 0-200 sccm range is fed through a closed-loop mass-flow controller. The ion pump of the growth chamber is isolated while a turbomolecular pump (1001 s^{-1}) is used to sustain a work pressure in the 1-130 mTorr range, as observed by a pirani-type gauge. Target ablation is completed by means of a KrF excimer laser ($\lambda = 248$ nm; 30 ns pulse width) focused on the target at 50° off the surface normal. Laser energy, deposition time and pulse repetition rate are fixed at 400 mJ (nominal), 5 min and 5 Hz, respectively. Considering the losses in one laser-window and one focusing lens, the fluency is estimated in $2 \,\mathrm{J}\,\mathrm{cm}^{-2}$ at the target surface. Most data reported in this work correspond to films deposited at room temperature.

3.2. Sample analyses

XPS data were collected after exciting the sample by an unmonochromatized Al K α line at 1486.6 eV. The energy scale was calibrated using thick films of cooper and silver, with lines at 932.67 eV for Cu_{2p_{3/2}} and 368.26 eV for Ag_{3d_{5/2}}. The high resolution XPS scans were completed at 0.2 eV energy steps and pass energy of 5.16 eV (constant}

pass energy mode). The measured full-width half-maximum (FWHM) for the Cu_{2p_{3/2}} line in metallic state with those settings is 1.6 eV. Additionally, survey scan were accomplished for every film in the 1400–0 eV energy interval at 1 eV per step, pass energy of 11.09 eV. To quantify the [N]/[Me] ratios the photo-ionization cross-section factor for the N_{1s} and main Me XPS-lines was considered. This value is fine-tuned by the λ_{MED} factor. This formalism was recommended by the NIST [18–22] and it is applied to calculate the relative sensitivity factors of N immersed in the respective Me-matrixes for our specific electron analyzer. The details of those calculations will be covered in a forthcoming publication.

EELS data were collected using an incident e-beam of 1200, a 0.5 eV per step and resolution of 2 eV, measured from the FWHM of backscattered electrons. For the AES measurements, the incident electron beam energy was set to 3200 eV, a resolution of 1.5 eV and 0.5 eV per step.

4. AES

4.1. AES N-KVV line shape

Figs. 1–8 show the KVV Auger peak line shape (in derivative mode, except Fig. 7) of nitrogen contained in different metals. The peak structures show good agreement with shapes reported in previous works for nitrides; see for example [23]. Notoriously, the N-KVV peak shape changes less as a function of nitrogen concentration in the films than the change it shows from metal to metal. This fact is exemplified in Fig. 9 with the Ru–N case. In that figure, we



Fig. 1. Shape of the N-KVV transition for nitrogen included in light metals (Be, B, and C).



Fig. 2. Shape of the N-KVV transition for nitrogen included in the Mg, Al, Si, and Ge metals.



Fig. 3. Shape of the N-KVV transition for nitrogen included in 3d-shell transition metals. There are important overlaps in the Sc-N, Ti-N, and V-N cases.



Fig. 4. Shape of the N-KVV transition for nitrogen included in Sr and 4d-shell transition metals.

can see that there are little modifications, not including the intensity, in the N-KVV basic shape as the deposition pressure is changed from 25 to 100 mTorr, at 25 mTorr steps. The same result is obtained using other metals; that is, the N-KVV basic shape is almost invariable in relation to the nitrogen concentration in films. Additionally, Fig. 10 shows the shape of the KVV Auger transition of nitrogen contained in amorphous and polycrystalline copper nitride. The crystalline status in these films was determined by X-ray and transmission electron diffractions. Again, the N-KVV basic shape is nearly invariable relating to the crystalline status of Cu_3N films. The same conclusion was achieved in other films.

First of all, the N-KVV line shape is influenced by the host matrix; subsequently, the N-KVV line shape can be used to typify metal nitrides. In Table 1, the AES information for nitrogen contained in the processed metals is summarized,



Fig. 5. Segment of the KVV transition for nitrogen included in Ag.

Table 1 Measured kinetic energies of the N KLL Auger transitions in nitrides

N immersed in	AES (kinetic energy, eV)							
	P ₁	P ₂	P ₃	P ₄	P ₅	P ₆		
Be	354.5	364	367.5	381	387.5	_		
В	351	361	-	381	-	-		
С	347	-	367	-	386	-		
Mg	356	366	372	381	386	_		
Al	352	363	-	383	-	-		
Si	350	363	-	383	-	-		
Sc	351	363.5	368	382.5	-	-		
Ti	352	361	-	382	-	-		
V	359	369	373	384.5	390	-		
Cr	357	367	372	383	389	_		
Mn	358	368	373	383.5	389.5	_		
Fe	357.5	367.5	373	383	389.5	_		
Co	357	368	373	383	389	_		
Ni	356	367.5	_	382	389	393		
Cu	357	367	_	380	386	391		
Zn	356.5	368.5	372.5	384.55	387.5	_		
Ge	352.5	366	370	383	-	_		
Sr	_	_	374	379.5	388	_		
Y	359	369	374	383	_	_		
Zr	361	370.5	375	384.5	-	392.5		
Nb	361	370	374.5	384	-	391		
Mo	359.5	369	373	385	-	391		
Ru	358	369	_	383	389	394		
Ag	_	_	_	380.5	385	391		
La	358.5	371	378.5	386.5	_	_		
Nd	_	_	376.5	385	389.5	_		
Yb	360	369.5	374.5	383.5	386	_		
Та	357	366.5	372.5	382	387	_		
W	357	368.5	372.5	384	387	_		
Re	358	369	_	384	387	391		
Pt	356	369	373	-	389	-		

Only the most prominent peaks are given (P_1-P_6) . The bold number represents the major peak.



Fig. 6. Shape of the N-KVV transition for nitrogen included in La, Nd, Yb, Ta, W, and Re metals.

where the energy of the most prominent negative peak (derivative mode) is emphasized in bold. Basically, the N-KVV Auger peak structure consists of a central peak, surrounded by satellite peaks on the low and high energy sides, where its position, number, and intensity differ according to the nitride nature. The peaks were classified in six categories, according to their relative positions. As listed in Table 1, P₁ is the lowest energy peak, and it is found in the 351–361 eV energy range. P₂ and P₃ are two closely related peaks, where P₃ often appears as a shoulder of P₂, making together a wide peak, like in Al–N, Cu–N, Zn–N, Ge–N, Mo–N, and Ru–N. P₂ occurs in the 361–371 eV interval, while P₃ appears between 368 and 378 eV. In most films P₄ is the central and major peak; typically it is found at 381–384 eV. On the high

energy-side two additional peaks emerge, P_5 and P_6 ; their shape has a remarkable structure in transition-metal nitrides. For instance in the Sc to Zn sequence, see Fig. 3, V–N starts developing a small shoulder in the P_5 position; in Fe–N and Co–N, P_5 is a well defined peak, forming a doublet with P_4 . Finally, in Ni–N and Cu–N, the structure is a triplet (P_4 , P_5 , and P_6). Note that in the Zn–N case the sequence is disrupted. To some extent, the same trend occurs in the next period, Fig. 4, since Mo–N shows a doublet structure similar to Cr–N, and Ru–N to Fe–N. In N contained in Ag, Fig. 5, the triplet structure is analogous to Cu–N, with inverted intensities; the most intense peak is now P_6 , instead of P_4 . It is not clear to conclude from the available data if the same trend occurs in the next period due to the open peak structures



Fig. 7. Direct mode AES spectra of In, Sn, and Sb with (a) and without (b) nitrogen. The arrow points to the N-KVV Auger transition, which is superimposed with the MNN transition of the corresponding metal.



Fig. 8. Comparison of AES spectra of films grown by ablating a platinum in (a) ultra-high vacuum and (b) at $P_{\rm N} = 100$ mTorr.



Fig. 9. Shape of the KVV transition of N contained in Ru as the deposition pressure changes from $P_{\rm N} = 25$ mTorr (a) to 100 mTorr (d). In this graph, it is evident that the N-KVV basic shape is almost invariable on regards to stoichiometry.

of the 5d-transition metals, although Ta–N clearly shows a shoulder in the P₅ position (see Fig. 6), being its structure similar to that of Co–N. In contrast, the 4f-transition metals display narrow N-KVV peak structures, comparable to that of Y–N, and their variations are very subtle in contrast to other transition metal sequences, although a small shoulder can be seen in the high energy region for Nd–N and Yb–N.

Another interesting point is the narrow structure and sharp peaks exhibited by Sr-N and Y-N, Fig. 4; here the ionic



Fig. 10. Comparison of KVV line shape of nitrogen contained in Cu₃N: amorphous film (a) and polycrystalline film (b). Film in (a) was prepared at room temperature and $P_{\rm N} = 100$ mTorr. Film in (b) was made at 200 °C and $P_{\rm N} = 115$ mTorr.

contribution to bonding is expected to be high. In Mg–N and Sc–N, where the ionic contribution to the bonding is significant, sharp-peak structures are also showed. In contrast, the covalent nitrides (for example B–N, C–N, and Si–N) have wide-peak structures.

From a practical point of view, the analysis of nitrogen contained in Ag, In, Sn, and Sb by AES is a very intricate issue. The complication stem from the superposition of N-KVV and Me-MNN transitions and it is accentuated by the high sensitivity of those metals, resulting in a barely perceptible nitrogen signal. Ag has its MNN transition spanning in the 250-360 eV energy range, however with carefully chosen acquisition parameters is possible to discriminate some region of the N-KVV transition, see Fig. 5. For nitrogen in In, Sn, and Sb, it results almost impossible to take apart the N Auger signal and the customary derived-mode of presentation is useless. Fig. 7 shows the 300-500 eV energy windows in direct mode for those cases. It can be seen that the N-KVV is completely superimposed with the MNN transition of the corresponding metal. In fact, in Sb-N, the nitrogen is perceived only if we compare carefully with the spectral characteristic of the pure element. In that case, it is fruitless to perform a fine structure analysis. Another elusive and peculiar nitride is Pt-N. In a recent work, the reaction of nitrogen with laser-ablated platinum was observed [24]; as a result, RPLD seems to be a suitable method to test the possibility of growing platinum nitride films. Fig. 8 shows the AES spectra of Pt ablated in ultra-high vacuum conditions and at P_N of 100 mTorr. The contrast clearly shows that nitrogen was incorporated in the film. This fact was corroborated by XPS and EELS. Once more, there is superposition of peaks; the N KLL signal is mixed with the Pt NOO signal resulting in a complex peak structure. Note the additional peak at 374 eV in Pt-N film, which is not present in the Pt film. Moreover, there is an increase of the intensity in the peak at 397 eV, which seems to be the result of superposition of the P_6 peak and the Pt $N_{II}O_IO_I$ Auger transition [25].

4.2. N-KVV line shape interpretation

It is recognized that the Auger transitions involving coupling of a core hole to one or two valence electrons have site specificity, being thereafter a potential tool to probe the local chemical environments [26]. One situation that catches our attention is the very little change in the N-KVV Auger transition as a function of the nitrogen concentration in films, see Fig. 9. If the Auger-electrons reflect the distribution of charge from the site they are emitted, then it follows that the local distribution of charge around N-sites is unaffected by the amounts of incorporated nitrogen. Then, the host lattice provides a screening effect, in such way that the N atoms do not 'perceive' any atom different than the host. Additionally, the N-KVV basic shape is, in essence, invariable between amorphous and crystalline films. Most probably, the local order around the N-sites is similar between amorphous and crystalline films, being the main difference the long-range



Fig. 11. Drawing of the interaction of d-transitional metals and N-orbital in octahedral sites. The Me d-orbitals shape two sets; one set able to hybridize with N p-orbitals to form bonding and anti-bonding states; while the leftover Me d-orbitals remain as non-bonding (to nitrogen) states.

order. We mention in the Section 1 that the octahedral sites in the receiver-lattice can be the favored sites due to packing factors; in those sites the N-atoms can be completely shielded by the Me-atoms. Providentially, Eberhart and MacLaren [27] anticipated an uncomplicated bonding scheme to understand the interactions of interstitial atoms in octahedral sites in a closed packed (d-transition) metal structure. In their model, see Fig. 11, the p-N orbitals should be arranged in the p_x , p_y , and p_z components, where (x, y) is some arbitrary plane and the z-axis is its normal. The d-Me orbital can be written in relation to that plane. As shown in Fig. 11, the σ and σ^* interactions are formed between hybridized p_z -N and d_z^2 -Me orbitals. The p_x -N and p_y -N hybridize with the d_{xz} -Me and d_{yz} -Me orbitals to give the π and π^* interactions. The d_{xy}-Me and d_{x²-v²}-Me do not hybridize with any p-N orbitals and produce a non-bonding δ -band in the gap between the hybridized orbitals. Following this scheme, the s σ -orbital can accommodate two electrons per Me–N pair. The mixed (p and d) σ - and π -orbitals can accommodate six electrons per Me-N pair, while the δ -orbitals can accommodate four electrons per Me–N pair. These hybridized orbitals will be filled following the exclusion principle of Pauli. Nitrogen provides a fixed number of valence electrons; consequently, the filling order will depend only from the partner atom. Thus, Me-N pairs with fewer d-electrons will have the low-energy orbitals filled. For example, in the B(III) group nitrides, ScN, YN, and LaN have the s σ -orbitals and the mixed σ - and π -orbitals filled to top [1,27,28]; the remaining, starting from the δ -band, are empty. As new d-electrons are incorporated, the leftover states from the δ -band start filling. That is, the nitrides of higher periodic groups will have electronic population in the middle-portion of the hybridized orbital structure. This will be the directive until the complete filling of the anti-bonding orbitals destabilize the local arrangement and nitrogen will be rejected from the octahedral sites; in that case less-dense

structures will be adopted where nitrogen is forced to assume a reduced coordination number. The results clearly show that the N-KVV Auger transition process is strongly influenced by the partner atom and that effect can be correlated to the proposed filling order. This is evident in d-transition metals, as it is shown in the sequences of Figs. 3, 4 and 6. In these metals, the intensities of P₅ and P₆ peaks show a relationship with the number of electrons in the d-orbitals. This phenomenon was previously reported in [29,30]. Salmerón and Baró [30] made the hypothesis that the KVV Auger process of non-metals adsorbed on transition metals is an interatomic process. They consider that the up and down electrons are originated in the d-band of the metal. Although this is a fair approximation, we consider that the up and down electrons are originated in the strongly hybridized orbitals around N-sites instead of the d-band of the metal. That is, we consider that the N-KVV Auger transition is still a localized effect where only the first neighbor atoms participate. Following the bonding-model of Eberhart and MacLaren [27] the charge distribution around N-sites is shaped by bonding interactions (BI), non-bonding interactions (NBI), and anti-bonding interactions (ABI). The filling order is first the BI, followed by filling of the NBI, and after everything else, the ABI. The Auger deexcitation processes of nitrogen can have the final hole in any state associated to those interactions, as it is shown schematically in Fig. 12. The atomistic Auger processes (K·L₁·L₁, K·L₁·L₂₃, and K·L₂₃·L₂₃) [30] develop into interatomic processes (K·BI·BI; K·BI·NBI; K·BI·ABI; K·NBI·ABI, and K·ABI·ABI), where the atomic energy levels are modified due to the interatomic interactions. Going back to results, note that according to the proposed filling order, the late-transitional-metal nitrides should have electrons in non-bonding states and some even in anti-bonding states; the intensities of P₅ and P₆ follow this trend as a function of the metal atomic-number. Then, we suggest that the intensities of P5 and P6 peaks are a direct



Fig. 12. Sketch of the interatomic Auger Me–N-KVV process. Peak (a) P_4 starts from Auger-electrons emitted from states generated by bonding interactions (BI), (b) P_5 from non-bonding interactions (NBI), and (c) P_6 from the anti-bonding interactions (ABI).

consequence of electronic population in non-bonding orbitals and anti-bonding orbitals, as it is shown schematically in Figs. 11 and 12. Interestingly, the stability of nitrogen of those films, like in Ag–N and Pt–N, are pointed by the high intensities of P_6 and P_5 peaks. Additionally, in Zn–N the sequence is disrupted. In the octahedral bonding scheme, a large number of Zn d-electrons will go to anti-bonding states; then, the occupation of octahedral sites by N in Zn is unfavorable. After that, it is supposed that N assume a minor coordination number, adopting configurations similar to covalent nitrides, maybe tetrahedral or trigonal planar. Note that in Zn–N, the N-KVV characteristic looks similar to Ge–N.

For the s- and p-shell nitrides, an equivalent bonding diagram can be constructed established in s-p hybrids. However, in that case the higher dispersion in energy of those orbitals does not permit to resolve them by using AES. In that case, the N-KVV structure present wide and open structures.

Some additional factors that might alter the Auger lineshape are the extrinsic losses suffered by the Auger-electron in leaving the solid. Extrinsic losses are those external to the Auger process such as those that result from an electron moving through a solid [31]. Inelastic scatterings and excitation of discrete collective oscillations of the electron gas (plasmons) are very probable extrinsic losses. In Fig. 13, the secondary electron background was removed by the Tougaard algorithm [32] for the N-KVV transition (in direct mode) for nitrogen contained in Nb, Mo and Cu. Numerical fittings by Gaussian functions permit us to speculate that the low energy peaks stem from energy losses of the P_{4-6}



Fig. 13. Interpretation of the KVV transition in direct mode of nitrogen included in Nb, Mo, and Cu. Solid lines correspond to 'true' auger transition, while dotted lines correspond to energy losses. Spectra are presented after elimination of background by the Tougaard algorithm [32].

main peaks since they can be made to (roughly) coincide with the losses measured in the EELS subsection. Note, however, that the energy losses in some nitrides is very intricate, being thereafter difficult to make comprehensive fittings and obtain the 'exact' shape of a particular Auger transition.

In conclusion, the AES spectroscopy when is applied to nitrides can be sensitive to bonding, non-bonding, and anti-bonding interactions between N and its partner element. The peak shape of the N-KVV in the high energy region is affected, in first instance, by the relative intensity of the 'true' Auger transitions (P₄₋₆); these are related to the abovementioned interatomic interactions. The peak structure formed by P₄₋₆ will be convoluted with the losses suffered by some Auger-electrons as they travel leaving the solid, shaping a complex peak structure in the low energy side region. Accordingly, the N-KVV Auger process seems to be responsive to the local distribution of charge around the N-sites.

5. Relation between the electron energy loss spectra of pure elements and nitrogen-containing films

The distinctive energy losses of electron beams going through or scattered from a solid surface can generate important information on the nature of the material under study [33,34]. EELS can give structural information similar to that provided by X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structure (EXAFS) [35]. In comparison with the two previous techniques, the main advantage of EELS is its accessibility; it can be carried out in laboratories with access to the basic electron spectroscopic techniques. In that case, EELS is



Fig. 14. Contrast between the EEL spectra of Be, B, C, Mg, Al, Si, Sc, and Ti pure-metals and nitrogen-containing films. C* denotes the graphitic form of carbon.

an ideal supplementary technique to AES or XPS. Despite that, a very limited number of papers are available making assessments of nitride formation by EELS. We believe that substantial information may be gained by using the characteristic energy-losses of known materials as "fingerprints" [35]. The fingerprint collection can be compared with the spectra of materials under study to obtain associations. This can be very useful in the case of interstitial compounds since the addition of interstitial atoms change profoundly the electron-energy-loss processes. Thereafter, the loss-spectra can be applied to unambiguously identify the interstitial atoms assimilation.

According to our experience, a very practical way of presenting the loss-spectra of nitrides is by presenting them side by side with the spectroscopic characteristic of pure elements [14]. The EELS spectra of studied material are presented in this way in Figs. 14-17. For convenience, the spectra are presented after linear background subtraction. Moreover, the intensity scale was amplified for most nitrides; this is necessary because of big differences in inelastic electron-scattering between nitrides and pure-elements. From the EELS results it is clear that the loss-structure changes for nitrogen-containing films with respect to pure-element films, indicative changes in electronic transport; this in turn is connected to changes in the atomic configuration. Here we can see that EELS has high sensitivity to detect those differences. For instance, in Pt-N films the nitrogen is observable in XPS or AES only by a detailed data accumulation of \sim 200 cycles, a time consuming task. In EELS, the data acquisition is performed in



Fig. 15. Contrast between the loss-spectra of pure-metals (V–Zn) and nitrogen-containing films.

10 cycles; less than 4 min, being the difference between the Pt and Pt–N films tangible.

We can see in the EELS results that the bulk-plasmon peaks reallocate its position. With some exceptions, like C–N and B–N, the position of the bulk plasmon tends to shift to higher energies in the nitrogen-containing films. One of the most studied nitrides by EELS are the CN_x , this



Fig. 16. Contrast between the loss-spectra of pure-metals (Ge, Sr-Mo, Ru, and Ag) and nitrogen-containing films.



Fig. 17. Contrast between the loss-spectra of pure-metals (In, Sn, Sb, La, Nd, Yb, Ta, W, Re, and Pt) and nitrogen-containing films.

is because the loss characteristics can identify the formation of high-density phases [12]. This is a good example of EELS examination. In the current work, the carbon films grown in vacuum, Fig. 14, show the two main features of graphite, energy losses at 27 and 6 eV, corresponding to the $\sigma + \pi$ and $\pi - \pi^*$ electron plasma resonance, respectively [36]. For the film grown in nitrogen environments, the $\sigma + \pi$ peak shifts from 27 to 23 eV and the $\pi - \pi^*$ peak is not well defined, due to the wide background of inelastic backscattered electrons. This implies that the C-N film produced has an atomic packing-density that is comparable to amorphous sp²-carbon films [37]. Furthermore, the fact that the high-energy region appears featureless, identify that we do not have high density β -C₃N₄-like compounds. By the decline on the plasmon energy, it is estimated a loss in mass density for C-N films of approximately 27 at.% with respect to the vacuum deposited graphite-like film. The same reasoning can be applied to the B-N film, which shows a decrement in the energy of the bulk-plasmon. Then, it is possible to conclude that the B-N films do not correspond to the high density phase of boron nitride. The same line of reasoning can be applied to the remaining nitrides, being possible to infer an augment in the atomic packing-factor in the largest part of nitrogen-containing films.

6. Core-level binding energies determined by XPS

In Table 2, the BE of the N_{1s} and the Me main line are listed for some nitrogen-containing films in its calculated stoichiometry. For comparison we have included the binding energy (BE) of 'similar' materials according to various references [38–64]. Fig. 18 shows a plot of the N_{1s} -BE for some of the processed nitrides ordered according to Me atomic-number. It is commonly accepted that the BE can be used to discern the predominant character in a particular bond, however the energy-span for nitride is very large, it goes form 395.4 to 400.1 eV for the processed metals here. Sr and La develop the most ionic species, while C, B, and Be, the most covalent. For most nitrides, it is not possible to



Fig. 18. N_{1s} binding energy in some nitrogen-containing films. This graph was assembled with data of Table 2.

Table 2 Nitrogen deposition pressure, calculated stoichiometries and BE of $N_{\rm 1s}$ and Me lines in the synthesized films

Nitride	Deposition pressure (mTorr)	Stoichiometry	Binding energy, this work (eV)		Binding energy ranges, as reported in previous works (eV)		References
			N _{1s}	Metal	N _{1s}	Metal	
Be–N	25	BeN _{0.66}	398.4	114.6 (1s)	N/A	N/A	_
B–N	50	BN _{0.86}	397.9	190.5 (1s)	398.1, 398.4	190.0, 192.2	[39-42]
C–N	75	CN _{0.33}	398.1, 400.1	284.6, 286.1 (1s)	398.2, 399.9	284.6, 286.5	[12,43]
Mg–N	50	MgN _{0.6}	395.5	50.2 (2p)	N/A	N/A	_
Al–N	25	AlN _{1.5}	397.0	74.2 (2p)	397.3	72.7, 74.4	[44-46]
Si–N	25	SiN _{1.4}	397.7	101.5 (2p)	397.4, 398.6	100.6, 102.34	[47–49]
Sc-N	2.5	ScN _{1.2}	396.3	$400.5 (2p_{3/2})$	396.1	400.4	[50]
Ti–N	25	TiN	396.6	455.2 (2p _{3/2})	396.9, 397.4	455.1, 457.6	[50,51–53]
V–N	50	VN	397.0	513.6 $(2p_{3/2})$	397.0	513.2	[50]
Cr–N	75	CrN _{1.2}	396.5	575.2 (2p _{3/2})	396.4, 396.8	574.4, 575.8	[50,54,55]
Mn–N	100	MnN	396.5	$640.5 (2p_{3/2})$	N/A	N/A	_
Fe-N	75	FeN	397.3	707.2 (2p _{3/2})	397.3	706.7	[56]
Co-N	120	CoN _{1.5}	396.8	778.4 $(2p_{3/2})$	396.6	778.4	[57]
Ni–N	100	NiN _{0.75}	398.1	852.9 (2p _{3/2})	N/A	N/A	_
Cu–N	100	CuN _{0.33}	398.0	933.4 $(2p_{3/2})$	397.0	932.86, 934.61	[58]
Zn–N	100	ZnN _{0.5}	397.4	1021.8 (2p _{3/2})	395.8	1022.0	[59]
Ge–N	75	GeN ₂	397.6	31.6 (3d)	397.4	1218.8 (2p _{3/2})	[44]
Sr–N	5	SrN _{0.33}	395.4, 397.2	133.8 (3d _{5/2})	N/A	N/A	_
Y–N	1	YN	395.9	156.3 (3d _{5/2})	N/A	157.4	[45]
Zr–N	15	ZrN _{0.88}	397.6	$180.0 (3d_{5/2})$	397.7	180.9	[53]
Nb–N	15	NbN _{0.73}	397.8	204.0 $(3d_{5/2})$	N/A	203.50	[63]
Mo–N	20	MoN _{2.57}	397.8	228.4 (3d _{5/2})	394.2	227.0, 228.1	[38,57]
Ru–N	50	$RuN_{1.1}$	397.9	$280.6 (3d_{5/2})$	N/A	N/A	_
Ag–N	100	AgN _{0.15}	396.8	368.3 (3d _{5/2})	N/A	N/A	_
In–N	100	InN _{1.2}	396.7	444.3 (3d _{5/2})	396.7	N/A	[60]
Sn–N	100	SnN _{0.30}	397.0	485.3 (3d _{5/2})	396.5	486.1	[61]
Sb–N	100	SbN _{0.5}	397.0	528.4 (3d _{5/2})	N/A	N/A	-
La–N	5	LaN _{1.38}	395.4, 397.2	833.4, 837.0 (3d _{5/2})	N/A	N/A	_
Nd–N	5	NdN _{0.81}	395.7	981.7 (3d _{5/2})	N/A	N/A	-
Yb–N	5	YbN _{0.83}	395.8	184.2 $(3d_{5/2})$	N/A	N/A	_
Ta–N	80	TaN	396.5	24.0 $(4f_{7/2})$	396.8	22.5, 22.85	[38,45,57]
W–N	100	WN ₂	396.9	32.9 (4f _{7/2})	396.9	32.7	[38,62]
Re–N	100	RN _{1.2}	397.2	41.6 $(4f_{7/2})$	N/A	41.8	[64]
Pt–N	50	PtN _{0.16}	397.70	71.3 (4f _{7/2})	N/A	N/A	-

make a clear distinction of the bonding character using the N_{1s}-BE as unique evidence. Even more, we observe convincing variations of core-level BE with respect to composition. For example, the value listed in Table 2 for W-N is 396.9 eV; it corresponds to nitrogen in WN₂. For W₂N the N_{1s} line appears at 397.5 eV. Similar dependencies with composition were observed in almost any of the processed metals. Observations made by Takano et al. [38] for metallic foils implanted with N confirm this behavior. That is, the N_{1s}-BE depend on composition for nitrides. As a result, the customary mode to typify a compound by its characteristic BE can be applied in nitrogen-containing films only if the precise elemental composition is known. For instance, we can observe some discrepancies between our data and previous reports, see Table 2. We believe that part of this problem has its root in poor nitrogen quantifications; thereafter the materials can have different stoichiometries.

On the other hand, the N_{1s} positions with respect to N^0 reveal that the N-atoms are always in electron-acceptor configuration, gaining electrons at expenses of Me-atoms.

This conclusion is obtained using as reference nitrogen physisorbed on graphite, with N_{1s} line position at 403.9 eV with respect to the Fermi level [65], or molecular nitrogen unperturbed by chemical bonds in gold films, with N_{1s} line at 402.7 eV [66]. As a result, the N_{1s} -BE in the 395.4–400.1 eV range is indicative of a charge transfer from Me to N. However, note that N_{1s} -BE is not particular to any Me–N bond, an interpretation often used in XPS data analysis but absolutely incorrect for nitrides. In conclusion, the N_{1s} -BE perceives the "global" chemical state of N-atoms in the Me-lattice.

7. Conclusions

From the presented Auger spectra of a large series of nitrogen-containing films, measured in situ, it can be concluded that the N KLL Auger transitions show features specific to the Me–N bonding. This transition is transformed in an interatomic process, in which the up and down electrons are originated in the Me–N hybridized orbitals around the N-sites. The large differences detected among them reflect the characteristic and multifaceted ways of bonding between nitrogen and partner element.

The EELS collection can provide a useful evidence of nitrogen assimilation in solids. The loss-processes are strongly affected by a change in the electronic configuration due to the integration of nitrogen atoms. The peak shiftings occur as a consequence of changes in electronic density; this is directly related to changes in atomic packing-factor. As a result, the loss characteristics can be used to assess or identify the nitride formation.

From the XPS analysis, it is possible to conclude that the shifting occurs as a consequence of changes in the chemical states. The N atoms are incorporated in an electron-acceptor configuration. The shifting of XPS-lines is a sign of charge transfer between the Me and N atoms. In contrast to AES, they are not sensitive to particular Me–N bonds.

The combination of XPS, AES, and EELS can be a very useful tool to distinguish the bonding present in nitrides.

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