Near edge x-ray absorption fine structure spectroscopy study of atomic nitrogen implanted in Al_2O_3 by low energy N_2^+ bombardment

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N_2^+ bombardment of Al_2O_3 has been investigated by near edge x-ray absorption fine structure spectroscopy. Two kinds of species were detected and were attributed to implanted nitrogen atoms and nitride species. These results are discussed in relation to previous attributions in the literature of these species to AlNO and AlN. © *2001 American Vacuum Society.*
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I. INTRODUCTION

Low energy ion implantation in metal oxides has been widely studied because of its fundamental and applied interest for the preparation of thin films and other technological materials.[1] Nitrogen (i.e., N_2^+) bombardment of metal oxides has been reported to produce changes in stoichiometry by substitution of oxygen by nitrogen ions.[2,3] Typically, the chemical state of this implanted nitrogen has been recognized as nitride species. Choi *et al.*[4,5] have recently reported that more than one type of nitrogen species is formed when Al_2O_3 is subjected to low energy ($0.5 < E < 2$ keV) ion bombardment. Based on the binding energy (BE) values of the x-ray photoemission spectroscopy (XPS) peaks of these species, Choi *et al.* assigned them to AlON (N 1s BE 402.5 eV) and Al–N (N 1s BE 396 eV). The first type of species is formed by low energy ion bombardment ($E \approx 0.5$ keV), while both of them are formed at $E \geq 1$ keV. Besides, a badly defined peak at 397.6 eV, which appears at intermediate values of bombarding energy, is attributed to Al–N. Very recently we have also reported these N_2^+ bombardment processes in Al_2O_3.[6] Basically this is a continuation of previous work by Bertoti *et al.*[7] on the same subject. In both cases we have found by XPS a behavior similar to that reported by Choi *et al.* However, our interpretation of the higher binding energy peak substantially differs from that of those authors. After a careful analysis of XPS and ion scattering spectroscopy (ISS) spectra in a similar ion implantation experiment, in which peak positions, intensities and thermal stability of these species were considered, we proposed that the peak should be attributed to atomic nitrogen occupying lattice and/or vacancy positions of an altered Al_2O_3 network.[6] In the same paper the appearance of a small O 1s peak at 537 eV upon O_2^+ bombardment was attributed to the formation of similarly trapped species of atomic oxygen.

With the aim of adding more support to this assignment we have carried out experiments by x-ray absorption spectroscopy (XAS) by recording the near edge fine structure (NEXAFS) spectrum of nitrogen implanted Al_2O_3 samples.

NEXAFS spectra of elemental atomic species of nitrogen implanted in solids are typically characterized by sharp resonance peaks.[8–10] So, in principle, their identification should be easy since the spectra are characterized by narrow sharp peaks, in contrast with the broader structure of typical nitride species.

II. EXPERIMENT

The XPS spectra of nitrogen implanted in Al_2O_3 were recorded on a Leybold–Heraeus LHS-10 spectrometer working in the pass energy mode at a value of 50 eV. The Mg $K\alpha$ line ($h\nu = 1253.6$ eV) was used as the excitation source. A reference for the BE scale of the spectra was taken at 284.6 eV for the C 1s peak of the carbon contaminating the sample. N_2^+ bombardment in the energy range of $0.5 < E < 2$ keV was carried with a Leybold–Heraeus hollow cathode ion gun (IQP-10). Bombardment was carried out for 30 min (total dose of 0.9 and 5.8×10^{16} ions cm^{-2} for 0.5 and 2 keV, respectively) up to saturation of the N 1s signals. A thorough XPS investigation of this N_2^+ bombardment process can be found in a previous paper.[6] After preparation the samples were exposed to air and stored without any special precaution. Apart from an increase in the intensity of the C 1s signal, no change in the shape of N 1s signals or in the relative intensity of spectrum components was detected by XPS after several weeks of exposure to air. However some attenuation of the Al 2p, O 1s, and N 1s signals was observed, as expected from this surface contamination by carbon. These samples were investigated by NEXAFS together with other untreated Al_2O_3 samples that were bombarded *in situ* in the ultrahigh vacuum (UHV) chamber used for the NEXAFS experiment. No noticeable differences in the shape of the spectra were detected for the *ex situ* or *in situ* samples subjected to nitrogen bombardment at the same energies, although the intensity of the signals was slightly smaller in the former case probably due to contamination of the surface.

NEXAFS spectra at the N K edge were recorded at the PM-1 beam line at the BESSY II synchrotron in Berlin (Germany). The photon energy was selected with a SX-700 plane grating monochromator and the spectra were recorded by
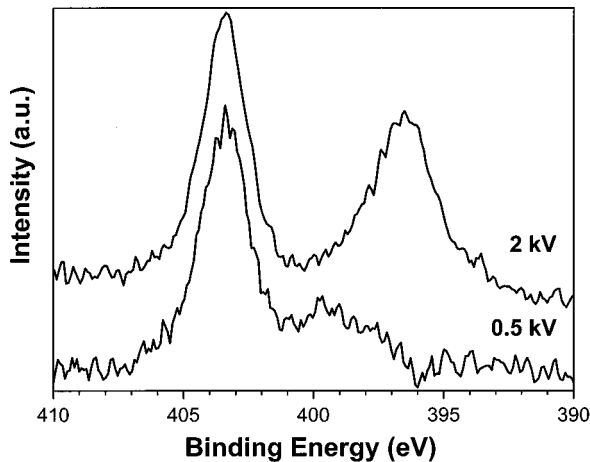
FIG. 1. XPS spectra of Al_2O_3 surfaces modified by N_2^+ ion bombardment.

FIG. 2. NEXAFS spectra corresponding to the two samples in Fig. 1.

total electron yield (TEY) by measurement of the drain current through the sample or by channeltron detection. Except for the background line, similar shapes were recorded for the spectra by these two methods of detection. Determination of photon intensity at each energy (i.e., I_0 measurement) was done by measuring the current with a gold grid placed in front of the samples. Spectra are represented after dividing the sample signal by this reference signal.

For NEXAFS analysis, the Al_2O_3 samples consisted of thin films (thickness ~ 0.5 μm) of this material deposited onto a metal substrate by plasma enhanced chemical vapor deposition (CVD). By XPS analysis either these thin film samples or α-Al_2O_3 single crystals were used. In both cases the XPS results obtained were quite similar. Thin film samples were preferred for XAS studies because they presented enough conductivity so to avoid undesired charging effects and to enable drain current recording of the spectra.

III. RESULTS AND DISCUSSION

Figure 1 shows N $1s$ photoelectron spectra for nitrogen implanted at 0.5 and 2 keV on Al_2O_3 thin films. These spectra are equivalent to those previously reported by Choi *et al.*[4,5] and by ourselves[6] for a similar bombardment experiment on α-Al_2O_3 single crystals. By low energy bombardment a N $1s$ peak at 403.4 eV is the majority species detected. Besides, a badly defined structure appears at lower BE. Meanwhile, by bombardment at the high energy, two peaks at 403.4 and 396.4 eV are clearly detected. In this second case the asymmetry on the high BE side of the 396.4 eV peak still suggests the presence of minority species with an intermediate value of BE. These two samples were then examined by NEXAFS spectroscopy and their corresponding spectra are shown in Fig. 2. In the sample bombarded with 0.5 keV ions a sharp peak at 398 eV with a full width at half maximum (FWHM) of ~ 1 eV is the most noticeable feature observable in the spectrum. This signal must have originated from the same nitrogen species as that producing the N $1s$ photoelectron band at 403.4 eV. Meanwhile, in the XAS spectrum of the sample bombarded with 2 keV ions this
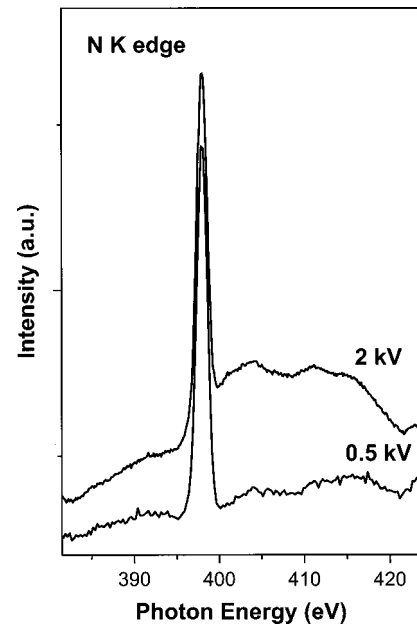
sharp peak, together with a much broader signal, is detected. This second signal is characterized by main maxima at around 404 and 411 eV and is similar to the N $1s$ NEXAFS spectra of nitride species reported in many metal nitride systems[11] (Note that these energy values refer to the approximate position of the maxima and not to the energies of the absorption thresholds and that, therefore, they cannot be directly compared with BEs of photoemission peaks). Some hints of a similar species can be also seen in the 0.5 keV spectrum. A small concentration of a species of that kind would agree with the appearance of a badly defined structure between 400 and 396 eV in the photoelectron spectrum of the 0.5 keV sample (cf. Fig. 1). However, additional investigations are still necessary to properly account for these small features.

Sharp resonance peaks of 1 eV width at the N K edge absorption spectra are not compatible with N–O species. Spectra of absorbed NO on metal surfaces are characterized by π^* and σ^* resonances at ~ 400 and 412 eV.[12] In nonoriented samples an average weighted intensity should be expected for these two resonances, a situation that is not found in our experiment with 0.5 keV. N K edge spectra of molecular nitrogen adsorbed on metals have also been reported.[13,14] Two features at 401, sharp and intense, and at 418 eV, broad and lesser in height, characterize this type of elemental nitrogen. The absence of any hint of this second feature at 418 eV in the spectrum of the 0.5 keV ion bombardment sample eliminates any suggestion that molecular nitrogen can be the species that cause the sharp feature at 398 eV. Steric hindrance of the incorporation of such molecular species within the aluminum oxide lattice is another reason to disregard it as responsible for the signal recorded. Thus, we attribute the sharp resonance line to atomic nitrogen species located in empty positions of the lattice. A similar sharp resonance has been reported by Soriano *et al.* for

N_2^+ bombarded Zr and Hf or for TiN heated in O_2 at high temperatures.[8,9] A few years ago, Jiménez _et al._ attributed the appearance of a sharp peak at 398 eV to nitrogen atoms in interstitial positions of sp^3 BN,[10] where only by outgassing at $T>1000$ K did removal of these species occur.

Thus, the present NEXAFS results support our previous assignment of the two XPS peaks at 403.4 and 396.4 eV to atomic (i.e., N) and nitride species of nitrogen implanted in Al$_2$O$_3$. It seems that at low energy (i.e., $E\sim0.5$ keV), nitrogen ions are not able to preferentially remove oxide ions from the Al$_2$O$_3$ lattice. However some nitrogen atoms may become incorporated within the very rigid Al$_2$O$_3$ network, likely at interstitial or vacancy positions. At a higher energy (i.e., $E\sim2$ keV) preferential removal of oxygen must occur, and their lattice positions become occupied by nitrogen in the form of nitride species (i.e., Al–N bonds). This latter effect occurs without precluding the occupancy of some interstitial sites by atomic nitrogen as indicated by the appearance of the two peaks in the photoelectron spectrum. It is also interesting that due to the high stability of these implanted species of nitrogen further _ex situ_ thermal and environmental characterization would be possible with regard to other properties such as optical, magnetic, etc. Progress is being made in our laboratory in that direction.

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