

Chemical changes of PNN ceramics induced by ion bombardment and characterized by X-ray photoelectron spectroscopy

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ABSTRACT

In this work, the surface composition and chemistry of perovskite PNN ceramics obtained from a columbite precursor were investigated using X-ray photoelectron spectroscopy. The PNN ceramics were bombarded with argon ions, after which the chemical state and composition were determined. The results show that the sputtering technique caused substantial changes in the chemical states of Pb and Nb, but no detectable change in the chemical state of Ni. Notably, ion bombardment led to the removal of absorbed oxygen species. Furthermore, the chemical composition of the PNN ceramics was altered by the sputtering process, where decreases in the atomic percentages of Pb and oxygen were observed, while increases in the atomic percentages of Ni and Nb were observed.

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1. Introduction

Ceramics based on the relaxor ferroelectric lead nickel niobate $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PNN) perovskite are widely employed in micro-electronics as multilayer capacitors, actuators, and components that operate via the induced piezoelectric effect [1–3]. Applications involving these materials vary with their mechanical, electrical, and piezoelectric properties, which depend on the composition and the nature of the defects in the sample. Several studies have focused on the microstructure [4], morphology [5], and electrical properties [6] of this material.

In practical electronic devices, the sputtering of noble gas ions is used to etch the surface of these materials [7]. Therefore, the chemical composition and chemical states of the surface must be precisely known. Zhu and Lu [8] used XPS to investigate changes in the chemical state and composition of the perovskite $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ system after bombardment with argon ions. These studies found a change in the chemical state only of Pb^{2+} to Pb^0 , with no concomitant change on the chemical states of Zr or Ti ions. Also, the atomic ratio of $\text{Pb}/(\text{Pb} + \text{Zr} + \text{Ti})$ was observed to decrease upon sputtering. Mukhopadhyay and Chen [7] studied the surface properties of the perovskites SrTiO_3 and $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and their

response to ion bombardment. Here, changes in the chemical states of Pb and Ti were observed, but no changes were observed for the other elements. Further, it was found that ion bombardment caused almost no change in the surface composition of SrTiO_3 , while that of PZT was substantially altered. Similarly, XPS studies by Kim et al. [9] revealed changes in the chemical behavior of PZT during argon ion bombardment. Specifically, it was found that the chemical states of Pb and Ti changed upon argon ion bombardment, while the chemical state of Zr remained constant. Also, the relative percentages of all elements were altered by ion bombardment due to the preferential removal of oxygen.

More recently, Singh et al. [10] used XPS to study the $\text{BaSn}_{1-x}\text{Nb}_x\text{O}_3$ system. The studies found no change in the chemical states of Ba and Sn, but the chemical state of Nb was reduced from Nb^{5+} to Nb^{4+} at high energy argon sputtering at 140 K, which disappeared at 298 K. Separately, Kurmar et al. [11] used XPS to investigate the changes of sintered barium titanate induced by argon ion sputtering. The studies found that the Ba spectra undergo subtle modification upon argon ion bombardment, and the titanium ions undergo a small fractional reduction of Ti^{4+} to Ti^{3+} .

These studies and others have shown that each chemical/substance responds to ion bombardment differently. To our knowledge, there are no prior reports of the influence of argon ion bombardment on PNN ceramics. Here, our attention focuses on changes in the surface properties of perovskite PNN ceramics induced by

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bombardment with argon ions. The influence of ion etching on the surface chemical composition and chemical states of the perovskite PNN ceramics are specifically investigated.

2. Experimental

2.1. Sample preparation

Pb(Ni_{1/3}Nb_{2/3})O₃ ceramics were synthesized using a methodology similar to the B-site precursor mixed oxide synthetic route, as reported earlier [12]. Details of the synthesis and sample preparation are described in a previous report [13]. The perovskite PNN ceramics were characterized by X-ray diffraction (XRD) before analysis by XPS.

2.2. XPS measurements

XPS spectra were collected using a PHI 5700 X-ray photoelectron spectrometer equipped with PHI 04091 neutralizer and a monochromatic Al K α X-ray source ($h\nu = 1486.7$ eV) incident at 90° relative to the axis of a hemispherical energy analyzer. The spectrometer was operated at high resolution with a pass energy of 23.5 eV, a photoelectron takeoff angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. The base pressure in the chamber during measurement was 1×10^{-9} Torr. After collection of the data, the binding energies were referenced by setting the C 1s binding energy to 284.8 eV. All peaks were fit with respect to spin-orbit splitting. Standard curve-fitting software (Multipak V5.0A; Physical Electronics, Inc.) using Shirley background subtraction and Gaussian–Lorentzian profiles was used to determine the peak intensities. The XPS results have been collected from non-sputtered and sputtered PNN ceramics with 0.5 keV argon ion.

3. Results and discussion

3.1. Changes in chemical states

From Fig. 1, the XRD pattern shows a 100% perovskite phase of Pb(Ni_{1/3}Nb_{2/3})O₃ that could be matched with JCPDS file no. 34-103, in agreement with a previous report [13]. Survey spectra of sputtered PNN ceramics showed the presence of all elements of the PNN ceramics, with no significant differences from that of non-sputtered surfaces that have been reported earlier [13] (data not shown). Figs. 2–5 show the narrow-scan XPS spectra of Pb, Ni, Nb and O core level, respectively. The line position of non-sputtered Pb 4f_{7/2} (Fig. 2a) appears at ~138.0 eV, which can be assigned to Pb²⁺ in the perovskite structure [14]. After sputtering with argon ion for 5 min (Fig. 2b), the second component corresponding to metallic Pb (Pb⁰) appears at ~136.5 eV, consistent with observations by Kim et al. [9], Mastelaro et al. [15], and Watt et al. [16]. The presence of metallic Pb can be attributed to the reduction of Pb²⁺ to Pb⁰, which

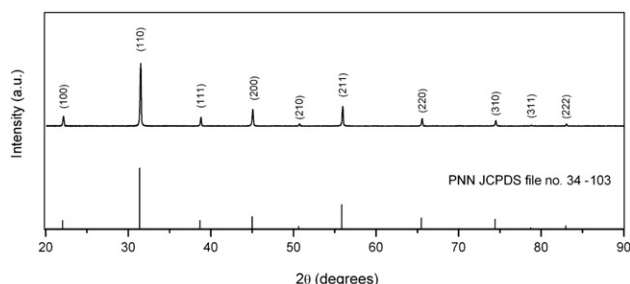


Fig. 1. The X-ray diffractogram of Pb(Ni_{1/3}Nb_{2/3})O₃ ceramics.

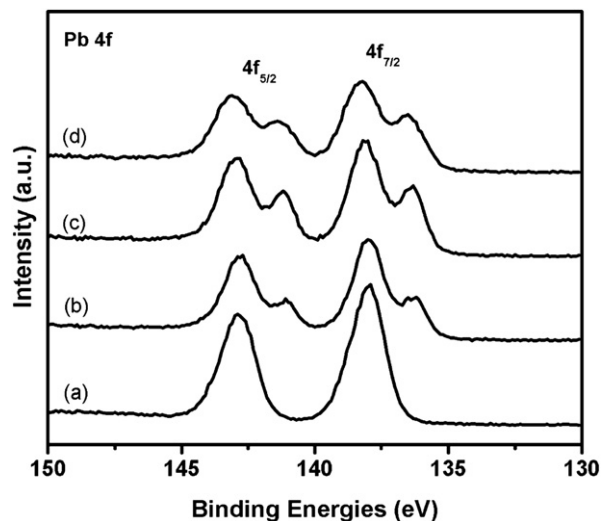


Fig. 2. Narrow-scan XPS spectra of Pb 4f for PNN ceramics (a) before Ar⁺ sputtering, and after Ar⁺ sputtering for (b) 5 min, (c) 15 min, and (d) 30 min.

is caused by the argon ion sputtering as earlier suggested by Mastelaro et al. [15]. The intensity of the latter component increases with sputtering time as shown in Fig. 2c and d.

The XPS narrow-scan spectrum of Ni 2p is presented in Fig. 3. The binding energy of Ni 2p_{3/2} for the non-sputtered sample (Fig. 3a) is ~855.3 eV, which is consistent with the value previously reported for the perovskite structure [17]. Fig. 3b–d shows the narrow-scan XPS spectra of Ni 2p for argon ion-bombarded PNN ceramics. The data demonstrate that no other component of Ni was observed here, but the intensity of the peak increases with sputtering time. This trend might indicate an increased relative concentration of Ni.

The XPS spectrum of Nb 3d for the non-sputtered ceramics is shown in Fig. 4a. The spectrum shows only one signal for Nb 3d_{5/2} at ~206.4 eV, which corresponds to Nb⁵⁺ in the perovskite structure [18]. After sputtering the sample for 5 and 15 min (Fig. 4b and c), slightly/almost no second peak of Nb 3d_{5/2} was detected. After sputtering the sample for 30 min (Fig. 4d), the Nb 3d_{5/2} peak shows asymmetry and broadening. The peak can be deconvoluted into two components. The first peak at ~207.2 can be assigned to Nb⁵⁺,

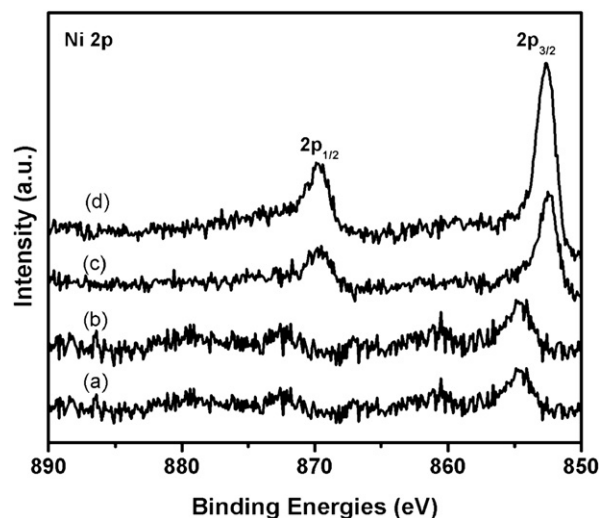


Fig. 3. Narrow-scan XPS spectra of Ni 2p for PNN ceramics (a) before Ar⁺ sputtering, and after Ar⁺ sputtering for (b) 5 min, (c) 15 min, and (d) 30 min.

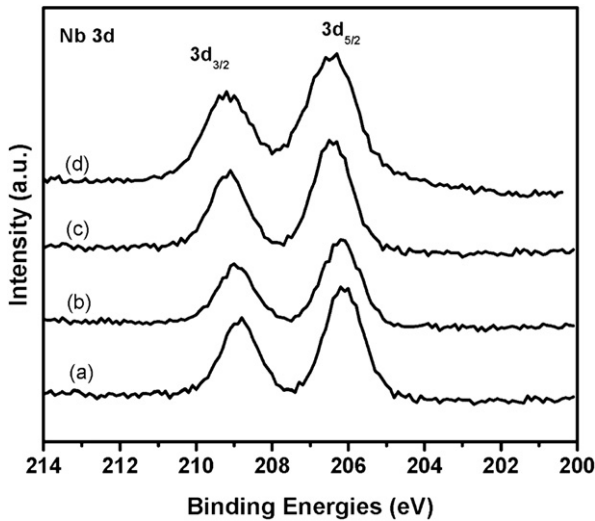


Fig. 4. Narrow-scan XPS spectra of Nb 3d for PNN ceramics (a) before Ar^+ sputtering, and after Ar^+ sputtering for (b) 5 min, (c) 15 min, and (d) 30 min.

while the second peak at ~ 205.6 eV suggests that Nb^{4+} was generated by a chemical reduction of Nb^{5+} to Nb^{4+} during ion bombardment, which can be regarded as sputtering-induced [10].

The narrow-scan of O 1s core level spectrum of a sintered sample in Fig. 5a shows two peaks, which agrees with studies reported by Pham et al. [19], Xia et al. [20], and Cho [21]. The first peak appears at ~ 529.5 eV, which is usually assigned to oxygen in the PNN lattice [22]. The second peak appears at ~ 531.4 eV, which might be attributed to absorbed oxygen species as suggested by several researchers who investigated similar perovskite ferroelectric ceramic systems [15,19,22]. After Ar^+ bombardment, the intensity of higher binding energy peak, which is assigned to hydroxyl absorbed species, decreases as a function of sputtering time. This trend indicates that the absorbed oxygen species can be removed by the sputtering process. A shift in the binding energy is also observed, which is in agreement with observations by Lu et al. [22].

From the overall results here, the interesting points are, first of all, that the sputtering process affects the chemical states of Pb and

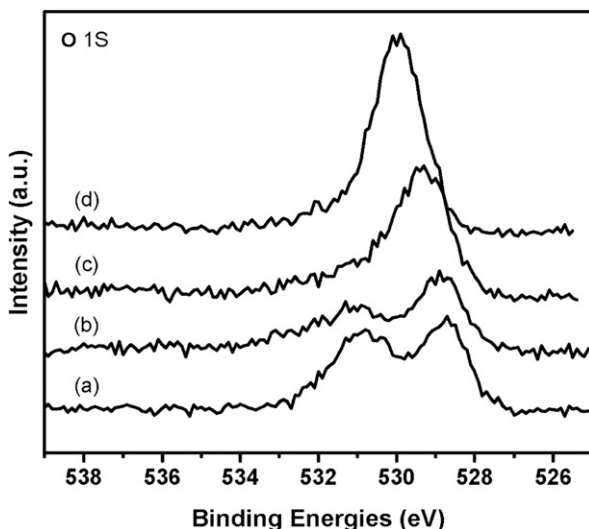


Fig. 5. Narrow-scan XPS spectra of O 1s for PNN ceramics (a) before Ar^+ sputtering, and after Ar^+ sputtering for (b) 5 min, (c) 15 min, and (d) 30 min.

Table 1

Atomic composition of the PNN ceramics before and after Ar^+ bombardment.

Sample	Atomic percentage			
	Pb 4f	Ni 2p	Nb 3d	O 1s
Before sputtering	22.3	1.4	8.6	68.7
After sputtering for				
5 min	29.8	4.5	9.8	55.9
15 min	26.9	8.2	13.8	51.2
30 min	17.6	10.5	22.8	48.1

Nb, but not the chemical state of Ni. Second, bombardment by argon ions can eliminate absorbed oxygen species. Third, it is easier to induce a change in the chemical state of Pb than it is to induce a change in the chemical state of Nb. This phenomenon might be due to the fact that the Pb–O bond is broken more easily than the Nb–O bond.

3.2. Change in chemical composition

Using sensitivity factors, the atomic percentages of the elements can be obtained from the area of each photoelectron peak. Using the Multipak Physical Electronics program, the surface chemical compositions of the PNN ceramics are shown in Table 1. Sputtering-induced changes in the chemical compositions are observed. In particular, the atomic percentages of Ni and Nb increase with the sputtering time, while those of Pb and oxygen decrease with sputtering time. These results are in agreement with those observed from PZT ceramics, where the sputtering process causes a decrease of Pb and oxygen percentages and an increase of Zr and Ti percentages [7]. The decrease in oxygen percentage is due to preferential removal of oxygen atoms [8,11]. The fractional concentration of Pb diminishes with increasing sputtering times due to the loss of Pb ions, since the sputtering process often generates heat. Lead is a relatively volatile component in the solid, which is known to evaporate during high temperature sintering of lead-based materials [2]. The decrease in the atomic percentages of Pb is likely responsible for the observed increase in the atomic percentages of Ni and Nb.

4. Conclusions

The XPS studies presented here show that the sputtering process can cause changes in both the chemical states and the chemical compositions of PNN ceramics fabricated via the columbite route. However, the sputtering process affects each element differently. The chemical states of Pb and Nb change due to the sputtering process, while that of Ni is unaltered. In addition, absorbed oxygen species are removed by the sputtering process. The chemical compositions of PNN ceramic can also be altered by the sputtering process. The compositions of both Pb and oxygen decrease, while those of Ni and Nb increase. Even though the sputtering process can be used to clean the ceramic surfaces, compositional and electronic changes induced by the sputtering might affect the electrical properties of the materials. These potential effects warrant additional investigation.

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