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# Hydrogen-induced atomic deformation in $SrBi_2Nb_2O_9$ perovskite structure

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The origin of hydrogen-induced structural deformation of ferroelectric $SrBi_2Nb_2O_9$ (SBN) thin films is investigated by annealing in forming gas ($3\%$ $H_2$–$97\%$ $N_2$). High resolution transmission electron microscopy and fast Fourier transformation analysis reveal that the {115} planes are shifted upward and downward by 0.92 Å along {115} plane after forming gas annealing, resulting in $(00l)$ planes inclined by 9.54°. This shifted distance of 0.92 Å means that the perovskite structure is distorted by 29.98% compared to the normal interatomic distance of 3.077 Å. This distorted perovskite structure results in degradation of ferroelectric properties. However, this lattice deformation and ferroelectric property of SBN films are recovered after annealing in oxygen ambient. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1815064]

Bi-layered perovskite thin films such as $SrBi_2Ta_2O_9$ (SBT), $SrBi_2Nb_2O_9$ (SBN), and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) have been extensively studied for the application of ferroelectric random access memories (FRAMs) because of large remnant polarization, low coercive field, low leakage current, and high fatigue resistance on Pt electrodes.[1–3] However, there are still some drawbacks such as process compatibility, degradation of ferroelectric properties during annealing process in forming gas (400–500 °C in a $N_2$ and $H_2$ mixture), reactive ion etching, and parasitic effects associated with electrical isolation and passivation. It has been reported for the past decade that the hydrogen annealing degrades ferroelectric properties and many published works have focused on the electrical-degradation mechanism of the ferroelectric capacitor. However, there are some controversial arguments for the origin of hydrogen degradation: the increase of leakage current,[4] the heavy peeling of electrode,[5] reduction of bismuth oxide to metallic bismuth,[6] or the formation of Bi–Pt compounds,[7] resulting in the hydrogen-induced degradation. Therefore, we need to trace the atomic structure focused on the exact same area before and after the hydrogen annealing and then, the origin of the hydrogen degradation should be understood with an atomic level. However, it is extremely hard to identify the atomic structure of the exactly same area with high-resolution transmission electron microscope (HRTEM). As a previous report by TEM study, Poonawala *et al.* suggested that the polarization degradation of hydrogen-annealed SBT capacitors is due to Bi loss from the SBT grains and near surface region.[8] It has also been observed that the grain size is decreased in the polycrystalline SBT thin films and at the interface of $SBT/Al_2O_3$ after forming gas annealing.[9,10] However, there has been no direct atomic-scale evidence of the hydrogen-induced deformation of lattice sites. In this study, we made a hole on the SBN/Si substrate by ion-milling method and observed the microstructural change of a SBN structure on a circular edge of the hole before and after the hydrogen annealing by HRTEM.

SBN films (200 nm in thickness) were prepared by spin coating of a metalorganic solution (0.1 mol/$l$, Kojundo Chemical Co.). Spin coating was done at 3000 rpm and rapid thermal annealing at 700 °C in oxygen ambient for 30 s followed drying step at 250 °C. SBN films were also grown on $Pt/Ti/SiO_2/Si$ substrates to confirm the hydrogen-induced electrical degradation and to recover its ferroelectric property by annealing in oxygen (note that HRTEM investigations were done with SBN films deposited on Si substrates). To crystallize the Bi-layered perovskite SBN structure completely, the samples were annealed at 700 °C for 1 hr in oxygen ambient. For electrical characterization Pt top electrodes with a diameter of 200 $\mu$m were deposited through a shadow mask. Generally, transparent region of conventional plane-view TEM sample is easily bended or broken during the subsequent annealing process. Therefore, in order to precisely trace the change of atomic structure of SBN films, we made a hole on a HRTEM sample using a short Ar-ion milling process. The circular edge of hole was almost transparent because the thickness is less than 5 nm and the transparent region was not damaged during the subsequent annealing process. The same HRTEM sample was annealed at 435 °C for 15 min in forming gas ($3\%$ $H_2$–$97\%$ $N_2$), followed by an oxygen recovery annealing at 600 °C for 15 min.

Figure 1 shows ferroelectric hysteresis loops of a Pt/SBN/Pt capacitor before [Fig. 1(a)] and after forming gas annealing, and after the oxygen recovery annealing. It shows clearly the hydrogen-induced degradation of ferroelectricity [Fig. 1(b)] and its recovery by following oxygen annealing [Fig. 1(c)]. As we have explained in previous work, this is probably due to the Bi–O bonds broken by the forming gas annealing and the broken Bi–O bonds are recovered again by the reaction of Bi and O in oxygen ambient during the oxygen recovery annealing.[11] However, we could not show any evidence for the atomic deformation due to the forming gas

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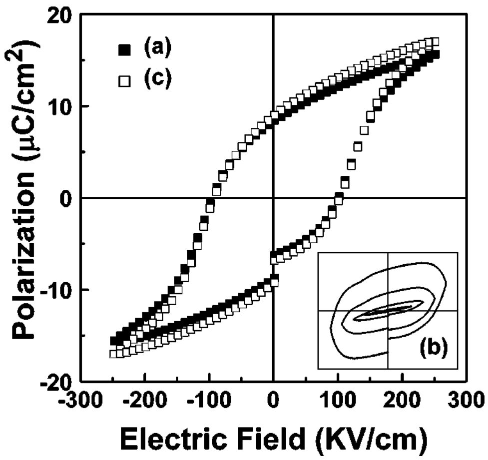


FIG. 1. Hysteresis loops of a Pt/SBN/Pt capacitor (a) before and (b) after forming gas annealing at 435 °C, and (c) after recovery anneal at 600 °C in the oxygen ambient.

annealing. In this work, we show the exact atomic structures by the HRTEM micrographs with a point-to-point resolution and the fast-Fourier transformation (FFT) lattice images before and after forming gas annealing, and after the oxygen recovery annealing. Figure 2 shows HRTEM bright-field micrographs and fast-Fourier transformation (FFT) lattice images of the same region of a SBN film taken before [Figs. 2(a) and 2(d)] and after forming gas annealing [Figs. 2(b) and 2(e)], and after the oxygen recovery annealing [Figs. 2(c) and 2(f)]. As one can see in Fig. 2(b), the (00*l*) fringes seen from bismuth oxide layers are distorted after forming gas annealing at the box region. This means that the atomic arrangement of SBN is destructed by the forming gas annealing and then, after the oxygen recovery annealing, this distorted lattice image of the box region is perfectly recovered to the original structure. Therefore, the (00*l*) lattice fringes are again revived [Figs. 2(c) and 2(f)]. In order to investigate the lattice image more precisely than the conventional HR-TEM image, we obtained FFT images with a Gatan Digital Micrograph software. Figures 2(d)–2(f) show the FFT images of the same region in Figs. 2(a)–2(c) (rectangular box), respectively. (The diffraction patterns are taken along the SBN $[1\bar{1}0]$ direction.) The dense vertical patterns originated from the long *c* axis of SBN, representing its typical crystal structure. However, after forming gas annealing, the (00*l*) spots disappeared and unknown spots tilted about 9.54° with respect to the (00*l*) spots appeared [Fig. 2(e)], although the (115) spots remain unchanged. However, after the oxygen recovery annealing, the FFT-diffracted patterns are recovered as shown in Fig. 2(f).

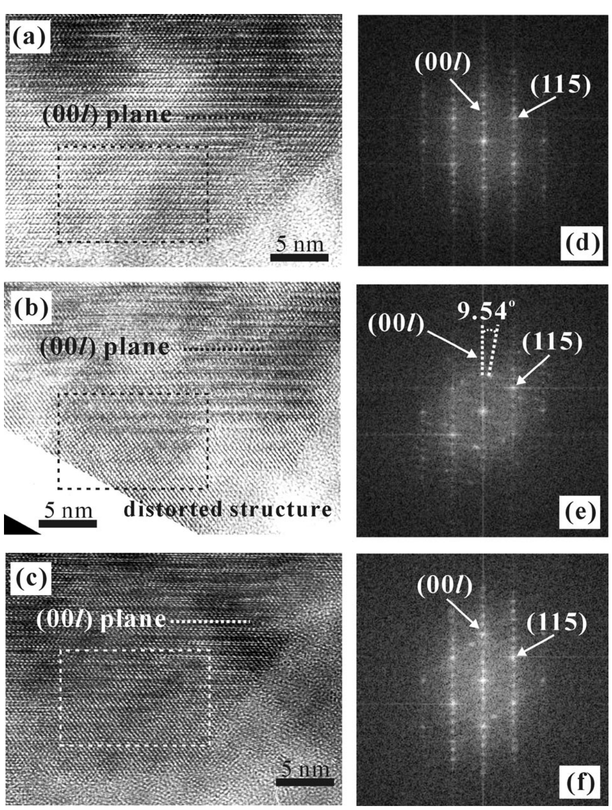


FIG. 2. Plane view HRTEM micrographs of a fresh SBN film (a), after forming gas annealing at 435 °C (b), and after oxygen recovery anneal at 600 °C (c). FFT images in (d)–(f) are taken in the box regions in (a)–(c), respectively.

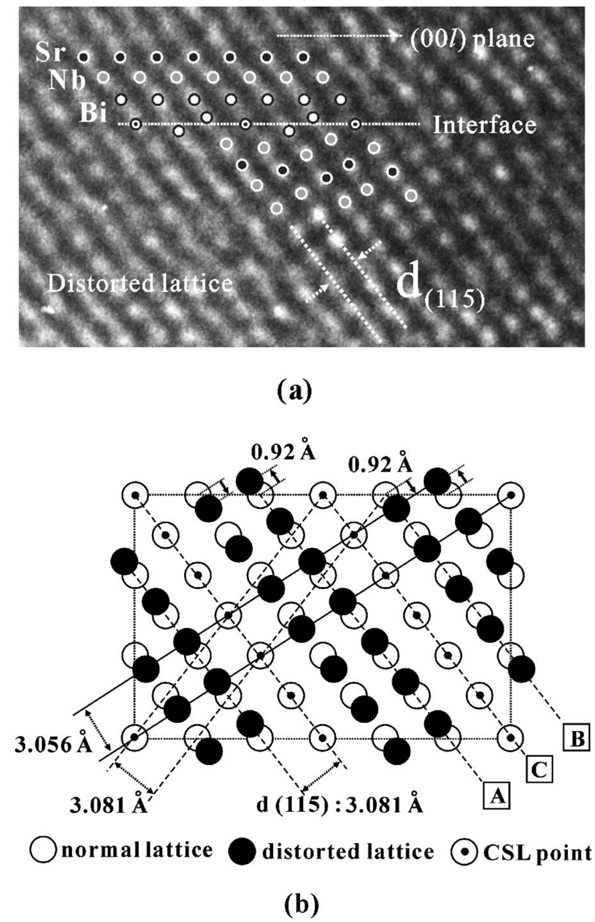


FIG. 3. (a) Enlarged HR-TEM micrograph and (b) its schematic atomic structure based on the HR-TEM image.

Figure 3(a) shows an enlarged HRTEM image of the annealed sample in hydrogen. It indicates an interface boundary between normal (00*l*) planes and distorted planes. From Fig. 3(a), we can draw a schematic lattice structure as shown in Fig. 3(b). In this figure, the interplane distance between {115} plane is 3.081 Å, which is not changed, but the distorted {115} interplane distance is reduced to 3.056 Å. In this model, the lattice sites of {115} planes which are denoted as lines A and B in Fig. 3(b) are shifted upward and downward by 0.92 Å along {115} plane. However, the coincident lattice site (CLS) of {115} plane denoted as line C is not shifted. The shifted distance (0.92 Å) means that after forming gas annealing the perovskite structure is distorted by about 29.98% of the interatomic distance (3.077 Å) along {115} planes, and this deformation could result in the degradation of ferroelectric properties of SBN films.

In conclusion, an origin of the hydrogen-induced deformation of SBN thin film was precisely investigated on the atomic level with HRTEM and FFT analyses. The HRTEM and FFT images show that the Bi-layered perovskite SBN structure begins to be deformed at the interface boundary layer and the lattice sites of {115} planes shifted up and downward while the coincident lattice sites remain at the original sites. These results are good to understand the hydrogen-induced degradation after forming gas annealing and oxygen recovery processes in the Bi-layered perovskite structure.

[1] J. F. Scott, M. C. Scott, C. A. P. de Araujo, and L. D. McMillan, Nature (London) **374**, 627 (1995).
[2] K. Watanabe, M. Tanaka, E. Sumitomo, K. Katori, and H. Yagi, Appl. Phys. Lett. **73**, 126 (1998).
[3] B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, Nature (London) **401**, 682 (1999).
[4] J. S. Lee and S. K. Joo, Appl. Phys. Lett. **81**, 3230 (2002).
[5] W. Hartner, P. Bosk, G. Schindler, H. Bachhofer, M. Mort, H. Wendt, T. Mikolajick, C. Dehm, H. Schroeder, and R. Waser, Appl. Phys. A: Mater. Sci. Process. **77**, 571 (2002).
[6] I. Koiwa, T. Kanehara, H. Kato, Sachiko Ono, Akira Sakakibara, T. Osaka, and K. Asami, Jpn. J. Appl. Phys., Part 1 **37**, 5192 (1998).
[7] R. Barz, F. Amrhein, Y. W. Shin, and S. K. Dey, Integr. Ferroelectr. **22**, 65 (1998).
[8] N. Poonawala, V. P. Dravid, O. Auciello, J. Im, and A. R. Krauss, J. Appl. Phys. **87**, 2227 (2000).
[9] S. Zafar, V. Kaushik, P. Laberge, P. Chu, R. E. Jones, R. L. Hance, P. Zurcher, B. E. White, D. Taylor, B. Melnick, and S. Gillespie, J. Appl. Phys. **82**, 4469 (1997).
[10] B. C. Lan, J. J. Hsu, S. Y. Chen, and J. S. Bow, J. Appl. Phys. **94**, 1877 (2003).
[11] I. S. Kim, Y. T. Kim, S. I. Kim, and I. H. Choi, J. Korean Phys. Soc. **43**, 850 (2003).