Growth atmosphere dependence of transport properties of NiO epitaxial thin films

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Recent possible applications in nonvolatile resistive switching memory devices renewed the interests in the transport properties of NiO. The variation on the conductivities of NiO films was reported to strongly affect the resistive switching phenomena. The conduction mechanism of NiO has been interpreted in terms of the bulk *p*-type conduction mechanism via Ni deficiencies ($Ni_{1-\delta}O$). Here we investigate the growth atmosphere dependence on the transport properties of NiO thin films epitaxially grown on MgO (001) substrate. The conductivities of NiO thin films showed completely an opposite tendency compared to the bulk *p*-type conduction mechanism. Microstructural analysis demonstrates that the conductivity of low temperature grown NiO thin films strongly correlates with tailing the band edge via the deterioration of entire film crystallinity rather than the grain boundaries including second phases. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2952012]

I. INTRODUCTION

NiO is an antiferromagnetic insulator and has been investigated to clarify the role of an electron correlation and/or a charge transfer on the insulating nature.[1] The antiferromagnetic properties have been utilized to investigate the magnetic interaction with ferromagnetic materials such as the exchange bias.[2] Other investigations have been concerned with sensing gases via the semiconducting properties[3] or the electrochromism utilizing the redox phenomena.[4] Recent possible applications in nonvolatile resistive switching memories renewed the interests in the transport properties of NiO.[5] As to the previous investigations on single crystal NiO, the *p*-type conduction via Ni deficiencies has been demonstrated.[6] The *p*-type conduction is enhanced with increasing the oxygen pressure and the formation temperature via increased Ni vacancies and the resultant holes.[5] In fact, the *p*-type conduction mechanism has been utilized to interpret the transport results of resistive switching NiO thin films.[5] In addition, the resistivity of NiO thin films before the resistive switching was found to strongly correlate with the resistive switching phenomena.[7] For example, Seo *et al.*,[5] Shima *et al.*,[8] and Jung *et al.*[9] found the significant effects of the ambient atmosphere during film deposition, including the oxygen content and the substrate temperature, on the resistive switching. Another interesting issue is the significant effect of the film crystallinity (polycrystalline or epitaxitial films) on the resistive switching regimes including a unipolar and a bipolar type.[10] Thus understanding the transport nature of NiO thin films would be invaluable for further understanding of complex resistive switching phenomena in NiO thin films. These backgrounds motivated us to investigate the growth atmosphere dependence on the transport properties of NiO thin films epitaxially grown on MgO (001) substrate.

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II. EXPERIMENTAL

NiO thin films were grown on MgO (001) single crystal substrate (d=4.211 Å) by pulsed laser deposition (ArF excimer λ=193 nm). NiO target was prepared by sintering NiO powders at 1350 °C for 24 h after milling the powders for 2 h. During the film formation, the ambient oxygen pressure was ranged from 10^{-3} to 10 Pa and the substrate temperature was varied from room temperature (RT) up to 800 °C.[11–13] The film thickness was varied from 30 to 420 nm with the constant growth rate of 0.86 nm/min. The crystal structures of resultant films were characterized by four-axis x-ray diffraction (XRD) measurement. The transport properties were measured by a four-probe method at 300 K. The optical absorption and transmittance were measured by UV-vis spectrometer. Atomic force microscopy (AFM) measurements were performed to investigate the surface morphology. High resolution transmission electron microscopy (HRTEM) measurements were also performed to study the microstructures.

III. RESULTS AND DISCUSSION

Figure 1 shows the reciprocal space map data and the phi scan around (113) peak. The NiO thin film was grown under 800 °C substrate temperature and 10 Pa oxygen pressure. The epitaxy of NiO thin film can be clearly seen. Since the lattice constant of bulk NiO is 4.177 Å, the NiO thin film receives an in-plane compressive strain from the MgO substrate with the lattice mismatch of 0.81%. Figure 2(a) shows the film thickness dependence on the c-axis lengths to investigate the strain relaxation. It can be seen that below 100 nm the compressive strain is gradually relaxed and approaching to the bulk value. Figure 2(b) shows the film thickness dependence on both the film resistivity at RT of the NiO thin films grown under 300 °C substrate temperature and 0.1 Pa oxygen pressure. There was no significant film thickness de-

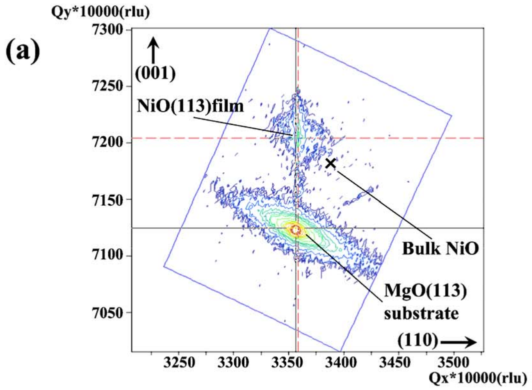

FIG. 1. (Color online) (a) Reciprocal space map and (b) the phi scan data around (113) of NiO thin films grown under 10 Pa oxygen pressure and 800 °C substrate temperature.

pendence on the film resistivity, indicating also the absence of the correlation between the film resistivity and the lattice constant. When performing four-probe electrical measurements for NiO thin films grown under the substrate temperatures ranged from RT up to 800 °C for various oxygen pressures, the resistivity of films grown above 400 °C was rather insulating and at least over 10^8 Ω cm at RT. Figure 3 shows the optical absorbance spectra when varying the oxygen pressure and the substrate temperature. It can be seen that the absorption edge tends to be broader as the substrate temperature and the oxygen pressure decrease. As shown in the inset XRD figure, the crystallinity tends to be deteriorated with decreasing the substrate temperature and the oxygen pressure. In addition, Table I shows the variations of the full width at half maximum (FWHM) at (002) and the film resistivity at RT for these films. Decreasing the substrate temperature and the oxygen pressure enhances the electrical conductivity. This trend is completely opposite when compared to the trend of the bulk *p*-type electrical conduction mechanism, since the formula $d=0.0107p_{O2}^{1/6}\exp(-9400/T)$ as to Ni vacancies (i.e., holes) in $Ni_{1-\delta}O$ has been reported.[6] Clearly the electrical conduction in the present study strongly correlates with the film crystallinity rather than the bulk *p*-type electrical conduction. Although these transport data are of relatively low temperature grown NiO films, understanding the transport properties of low temperature grown NiO films is important for the practical process combinations in the resistive switching memory applications.[5] As such understanding the transport nature of such low temperature grown NiO films would be valuable.

There are several possible mechanisms to interpret the variation on the electrical conduction of NiO thin films. The first possible scenario is based on the electrical conduction via the grain boundaries as reported elsewhere.[14] In fact, the electrical conduction through such grain boundaries has been discussed in the resistive switching studies of NiO thin films.[15] If the presence of such grain boundaries is responsible for the electrical conduction, the number of the grain boundaries should increase with the increase in electrical conductivity. To investigate the presence of such grain boundaries, HRTEM measurements were performed. Figure 4 shows the HRTEM images for thin films grown at 300 °C when varying the oxygen pressure from 10^{-3} to 10 Pa. The low magnification images show the smooth surface of the thin films. Although the high magnification image of film grown under 10 Pa oxygen pressure shows the grainlike surface morphology especially for the film grown under 10 Pa oxygen pressure, the height variation of the grains is ranged below 5 nm, which is obviously much smaller than the observed lateral surface morphology size. This was also confirmed by AFM measurements. In addition, the presence of the grains and the grain boundaries including the secondary phases cannot be identified at all by detailed analysis on all cross-sectional images. All selected area electron diffraction (SAED) patterns in the inset show the epitaxy of the fabricated thin films. Since the HRTEM analysis can give detailed microstructure information of the NiO thin films, above results indicate the absence of the grain boundaries including the secondary phases within the present epitaxial NiO thin films. Therefore, the scenario based on the presence of grain boundaries with the secondary phases alone cannot explain the observed trend on the electrical conduction of NiO thin films.

The other possible scenario is based on tailing the band edge via the degradation of the entire film crystallinity due to crystal defects and disorders.[16] It is well known that an in-

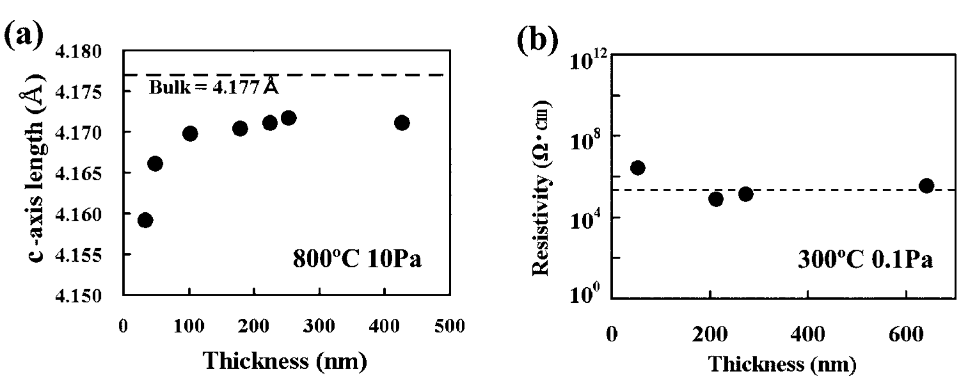

FIG. 2. (a) Film thickness dependence on the *c*-axis lengths of NiO thin film grown under 10 Pa oxygen pressure and 800 °C substrate temperature. (b) The film thickness dependence on the resistivity of NiO thin films grown under 0.1 Pa oxygen pressure and 300 °C substrate temperature.

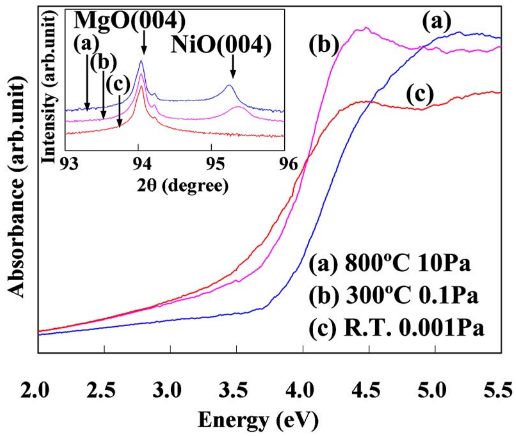

FIG. 3. (Color online) UV-vis absorption spectra of NiO thin films when varying the growth atmosphere. The inset shows the XRD data of the films.

sulator tends to be gradually conductive, as the crystallinity tends to be amorphous.[17] Also it is well known that high concentration of crystalline imperfections or defects in semiconductors create band tails in the distribution of the density of state.[18] The reason for this is that as the distances between defects become small, their energy levels broaden into bands. These bands then merge with the nearest parent bands of the extended states. If this scenario was appropriate, there should be a certain relationship between the crystallinity (e.g., FWHM) and the electrical conductivity. Figure 5 shows the oxygen pressure dependence on the resistivity of NiO thin films grown under 300 °C. It can be seen that the resistivity systematically increased with increasing the oxygen pressure, which is completely the opposite tendency compared to the bulk *p*-type conduction trend.[6] Figure 5 also shows the variation of FWHM at (002) for these films. FWHM decreases by increasing the oxygen pressure, indicating the degradation of the crystallinity by decreasing the oxygen pressure. There is a clear correlation between the entire film crystallinity and the electrical conduction. Therefore the electrical conduction of low temperature grown NiO thin films strongly correlates with tailing the band edge via the degradation of the crystallinity, as seen in Fig. 3. In many resistive switching oxides, the significant role of oxygen vacancies has been demonstrated with the electrochemical phenomena since such oxygen vacancies result in the *n*-type electrical conductions in many transition metal oxides. Although the resistivity of present epitaxial NiO thin films decreased drastically from 10^7 to 10^2 Ω cm when reducing the oxygen content, the *n*-type electrical conduction in NiO films seems to be not feasible even in the presence of the oxygen vacancies.[19] The major differences between our interpretation and the previous mechanisms[5,6] are the following two experimental findings: (1) the opposite trend of the oxygen

TABLE I. Resistivity and FWHM of the NiO films grown at various atmospheres.

	800 °C 10 Pa	300 °C 10^{-1} Pa	RT 10^{-3} Pa
Resistivity (Ω cm)	Over 10^8	3.24×10^5	3.84×10^3
FWHM (degree)	0.090	0.206	⋯

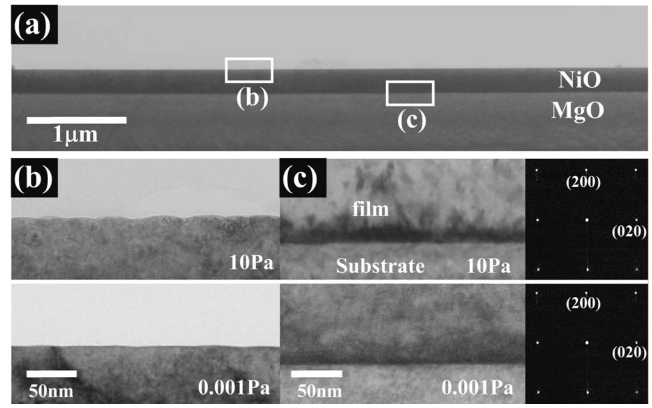

FIG. 4. Cross-sectional HRTEM images of NiO thin films grown at 10^{-3} Pa and 10 Pa oxygen pressures under 300 °C substrate temperature. Image (a) shows the low magnification image of the film. In (b), the images near the surfaces are shown. In (c), images near the boundary between the film and the substrate, and the SAED patterns are shown.

pressure dependence of the NiO film resistivity compared to the trend of the bulk *p*-type conduction mechanism formula and (2) the absence of second phases including metallic nickel phases within our films. Although antiphase boundaries, dislocations, and twins exist within the films, the correlation between bulk information, including XRD and spectra, and the electrical conduction indicates the minor contributions of such local crystal defects on the transport properties. The present study highlights that the degradation of the crystallinity rather than the bulk *p*-type conduction and local phases is crucial to interpret the transport properties of low temperature grown NiO thin films. This knowledge as to the significant crystallinity effect on the resistivity would be valuable to interpret the resistive switching effects in NiO thin films especially when the local stoichiometry is modified via applying the electric field.

IV. CONCLUSION

We investigated the transport properties of NiO thin films epitaxially grown on MgO (001) substrate when varying the ambient atmosphere. The electrical conductivity of the fabricated NiO thin films showed an opposite tendency compared to the general trend of bulk *p*-type conduction mechanism. Microstructural analysis demonstrated that the

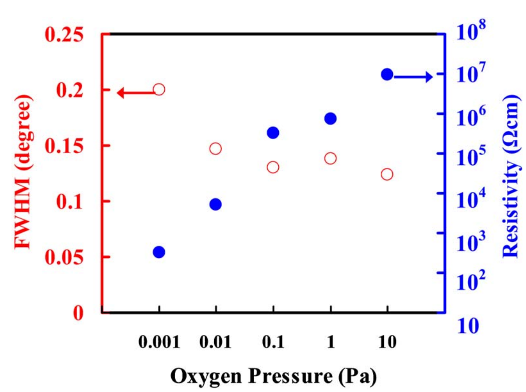

FIG. 5. (Color online) Correlation between the resistivity and the FWHM at (002) in the NiO thin films grown under 300 °C substrate temperature with varying the oxygen pressure.

electrical conduction of NiO thin films strongly correlates with tailing the band edge via the degradation of the entire film crystallinity rather than the grain boundaries including secondary phases and the bulk *p*-type conduction mechanism.

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