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Low-temperature magnetoresistance of Nb-doped TiO_2 transparent conducting films

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ABSTRACT

The magnetoresistance of two anatase Nb-doped TiO_2 films has been measured. The samples reveal both negative and positive magnetoresistance component at all measuring temperatures. It is indicated that the Lorentz force effect based on a two-band model can describe the positive magnetoresistance contribution well. Rather than weak localization or Kondo effect, the negative magnetoresistance behaviors follow a semiempirical expression considering the effect of localized magnetic moments. This expression, due to Khosla and Fischer in a paper published 40 years ago [R.P. Khosla, J.R. Fischer, Phys. Rev. B 2 (1970) 4084], is deduced from the s–d exchange Hamiltonian by considering the third-order perturbation. The field dependence of the magnetization curves for both samples reveals ferromagnetic characteristics, which proves the existence of localized magnetic moment in $Ti_{1-x}Nb_xO_2$ compounds.

In the last decade, significant attention has been focused on transparent conducting oxides (TCOs) both in fundamental research and in device applications due to their good combination of high electrical conductivity and excellent optical transparency [1,2]. Among various TCOs, indium tin oxide (ITO), Al-doped or Ga-doped ZnO, and Sb-doped or F-doped SnO_2 are those used most often in the field of flat displays, solar cells and architecture. However, due to the limitations of the existing materials (such as indium), as well as application to new devices, it is becoming increasingly difficult to satisfy the demand of the TCO market using only ITO, doped ZnO and SnO_2. Recently, Nb-doped TiO_2 (NTO) has been found to be a promising TCO material with resistivity of $\sim 10^{-4}\ \Omega$ cm and high transmittance of 95% in the visible region [3]. Liu et al. also confirm that NTO is an intrinsic transparent conducting metal according to its electronic structure by first-principle calculations [4]. Considering the growing significance of NTO and much of the work on the conductive mechanisms in TCOs being empirical, it is of significance to investigate the electrical transport mechanisms of NTO.

Besides the temperature dependence of resistivity, low-temperature magnetoresistance (MR) measurement is a power tool to diagnose the scattering mechanisms in these materials. To extract the quantum-interference process in disorder systems, low-temperature MR measurements have been carried out in various materials, including normal metals, superconductors, and semiconductors [5]. For ITO [6] and B-doped ZnO [7], relative systematical low-temperature MR measurements have been carried out, and it was found that the electron–electron interaction plays a key role in the two compounds at low temperature. In this work, we measured the low-temperature MR of two anatase NTO samples. It is found that the MR of NTO films consists of both negative and positive components, and the scattering due to the localized magnetic moment and Lorentz force are responsible for the negative and positive components, respectively.

$Ti_{1-x}Nb_xO_2$ films with $x = 0.15$ (Sample A, 420 nm) and $x = 0.05$ (Sample B, 450 nm) were deposited on (100) $LaAlO_3$ (LAO) substrates by a radio-frequency sputtering method. The target used in the sputtering process was prepared by a traditional ceramic process. TiO_2 and Nb_2O_5 powders with 99.99% purity were mixed in proper ratios, and then ground by ball milling for 12 h. The homogenous mixture was pelletized, pressed into a disc, calcined at 1303 K for 24 h in air and then furnace cooled. To prevent the contamination of magnetic ions, we used a polyurethane pot and some agate balls in the milling process. In addition, we chose copper instead of iron or stainless steel as the target shield during the deposition process and sealed all the samples as soon as they were taken out of the sputtering system. After the target was mounted to the sputtering gun, a pre-sputtering process of ~6 h was carried out to clean the surface of the target. The pre-sputtering process also carried out for 20 min in each deposition round. In all the measuring processes mentioned below, plastic tweezers were used to mount or unload the samples. Sample A and Sample B were deposited at 998 K and 1023 K, respectively. Details of the growth of the films have been published elsewhere [8]. The thicknesses of the films were mea-

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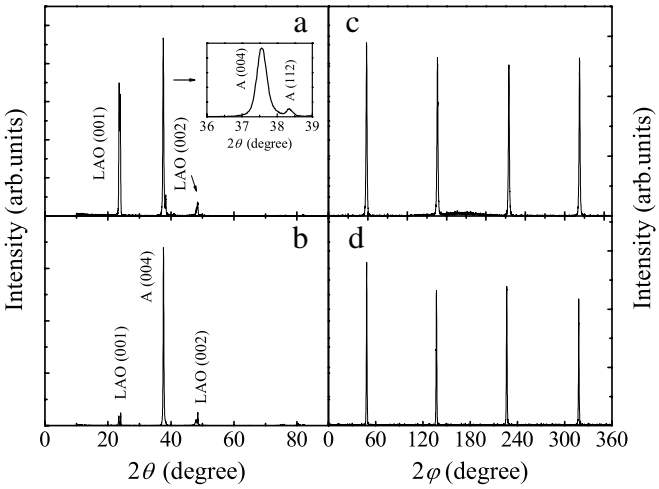

Fig. 1. XRD 2θ spectra for (a) Sample A and (b) Sample B, and XRD φ-scan spectra for (c) Sample A and (d) Sample B.

sured using a surface profiler (Dektak, 6m). The crystal structure and phase characterization were determined by a Rigaku D/max-2500v/pc X-ray diffractometer using Cu Kα radiation at room temperature. The electrical resistivity and Hall effect measurements were determined in a physical property measurement system (PPMS-6000, Quantum Design) by the standard four-probe method and four-point method, respectively. Magnetic measurements were done using a vibrating sample magnetometer equipped in the PPMS.

The X-ray diffraction (XRD) spectra of NTO films are shown in Fig. 1. Both samples are anatase (004)-orientated phase without impurities such as Nb_2O_5 and Ti_nO_{2n-1}. For Sample A, besides the sharp anatase (004) peak, a small anatase (112) peak also appears (Fig. 1(a)). In addition, in the φ-scan spectra, some tiny weak peaks are also found among the four uniform-distribution peaks (Fig. 1(c)) which indicate that Sample A is not perfectly epitaxially grown. As for Sample B, both the 2θ-scan spectra (Fig. 1(b)) and the φ-scan spectra (Fig. 1(d)) confirm the epitaxial growth of the (004)-orientated anatase phase.

Fig. 2 displays the magnetic field dependence of MR ($\Delta\rho/\rho_0$) up to 40 kG at different measuring temperatures for Sample A and Sample B. For Sample A, the MR versus field curves clearly consist of both negative and positive components. For Sample B, although only negative MR can be observed in the curves, the positive component cannot be ignored (see further remark below). Generally, several mechanisms are responsible for the positive MR in materials. Due to the different effective mass and relaxation time of the charge carriers, the Lorentz force on the carriers makes a positive contribution on the MR [9]. The spin–orbital interaction [10] and the Maki–Thompson superconducting fluctuation effect [11] also make positive contributions to the MR. Since superconductivity has not been observed in NTO thus far and the spin–orbital interaction only dominates at low field (<1.5 T), the positive part of the MR in our NTO films is not induced by these two effects. On the other hand, several reasons, including the weak localization effect [5–7] caused by the self-interference of wave packets when they are coherently back-scattered by impurities and the Kondo effect [12,13] caused by enhanced spin scattering of carriers by localized magnetic moments on lowering the temperature, can induce a negative MR. Considering that the thickness of our films is around 450 nm, we fit our experimental data of both samples with three-dimensional weak localization theory [5,14,15]; however, it is found that the theoretical prediction deviates greatly from the experimental data. When the contribution of the Lorentz force (see Eq. (5)) is considered [7], such deviation still exists. Thus, weak

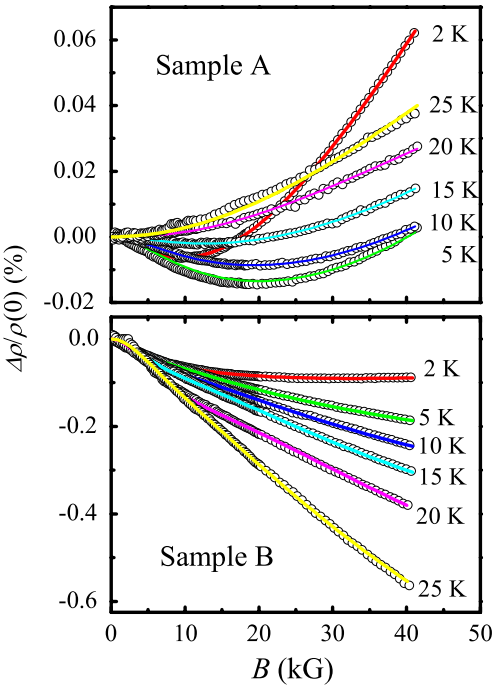

Fig. 2. (Color online) Low-temperature magnetoresistance versus magnetic field for Sample A (top panel) and Sample B (bottom panel). The solid lines represent least-squares fits to Eq. (6), and the open circles are the experimental results. For distinguishing, the experimental data of Sample B measured at 10 K, 15 K, 20 K and 25 K are 1.2, 1.5, 1.8 and 3 times amplified, respectively.

localization is inapplicable for describing the transport mechanisms of negative MR in our NTO samples.

To determine whether the negative part of the MR originates from the Kondo effect, we measured the resistivity variation with temperature from 2 to 300 K, and the results are presented in Fig. 3. The overall resistivity of both samples increases with increasing temperature, and such metallic behavior is consistent with the results of the band structure calculation [4]. For Sample A, as is shown in the inset of Fig. 3, the temperature coefficient of resistivity (TCR) becomes negative below 18 K, whereas the TCR of Sample B remains positive even when the temperature is reduced down to 2 K. As mentioned above, the XRD spectra show that Sample B is an epitaxial growth film along the [100] direction of LAO single crystal, while Sample A is not a perfect epitaxial film. In addition, the doping level of Sample A is far higher than that of Sample B. Hence the disorder level of Sample A is higher than that of Sample B, which might be the main reason that the resistivity of Sample B increases with decreasing temperature while the resistivity of Sample A varies in a opposite trend below 18 K. Most early reports suggest the negative TCR of TCO films at low temperature is an indication either of the Kondo effect [12] or of weak localization [6,7]. However, we find the resistivity of Sample A below 18 K is neither $\ln T$-dependent (an indication of the Kondo effect or two-dimensional weak localization) nor $T^{-1/2}$-dependent (an indication of three-dimensional weak localization). Therefore, the Kondo effect is also excluded as the origin of negative MR for both our NTO films. Hall effect measurements reveal that the carrier concentrations are independent of temperature from 300 down to 2 K; the values are 1.5×10^{21} cm^{-3} for Sample A and 5.5×10^{20} cm^{-3} for Sample B, respectively. According to first-principle calculation results, the Fermi level of anatase Nb-doped TiO_2 is located in the conduction band and reveals a metallic characteristic in the electronic structure [4], so the observation that the carrier concentration remains constant over the whole temperature range is physically reasonable.