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Variable range hopping in TiO_2 insulating layers for oxide electronic devices

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TiO_2 thin films are of importance in oxide electronics, e.g., Pt/TiO_2/Pt for memristors and Co-TiO_2/TiO_2/Co-TiO_2 for spin tunneling devices. When such structures are deposited at a variety of oxygen pressures, how does TiO_2 behave as an insulator? We report the discovery of an anomalous resistivity minimum in a TiO_2 film at low pressure (not strongly dependent on deposition temperature). Hall measurements rule out band transport and in most of the pressure range the transport is variable range hopping (VRH) though below 20 K it was difficult to differentiate between Mott and Efros-Shklovskii's (ES) mechanism. Magnetoresistance (MR) of the sample with lowest resistivity was positive at low temperature (for VRH) but negative above 10 K indicating quantum interference effects. [doi:10.1063/1.3682346]

I. INTRODUCTION

TiO_2 is a key material for oxide electronic devices because of its superior optical, electrical and magnetic properties.[1–7] In memristor devices, TiO_2 has become a very important field-tunable layer in between metallic electrodes, where the insulating property of the film is overcome by field induced anionic defect dynamics.[8] In a Co-TiO_2/TiO_2/Co-TiO_2 spintronic heterostructure where the electrodes are ferromagnetic, the role of TiO_2 is a pure insulator.[9] However, in the fabrication process of these devices the layers see different oxygen pressures during their growth which may influence their insulating properties. In this paper we study the weak transport properties of pure TiO_2 prepared by pulsed laser deposition (PLD) at different oxygen pressures. Much to our surprise, for the samples prepared between 650-750°C, we discovered a sharp minimum in the resistivity as a function of oxygen pressure centered at $\sim 1.4\times 10^{-5}$ Torr (mediated by defects) with variable range hopping (VRH) in most of the measured regimes. As the defects in TiO_2 (anionic and cationic) depend on the oxygen pressure, their effect on the VRH becomes crucially important not only for the fundamental understanding, but also for wide spread applications of TiO_2.[10] We have studied in detail the nature of TiO_2 transport at and around this resistivity minimum via temperature dependent electronic transport, magneto transport and Hall measurements.

II. EXPERIMENTAL SECTION

Epitaxial TiO_2 films were deposited by PLD on single crystal $LaAlO_3$ (LAO) substrate. The target was made by pressing and sintering TiO_2 (99.999% purity) powders. During the experiment, a

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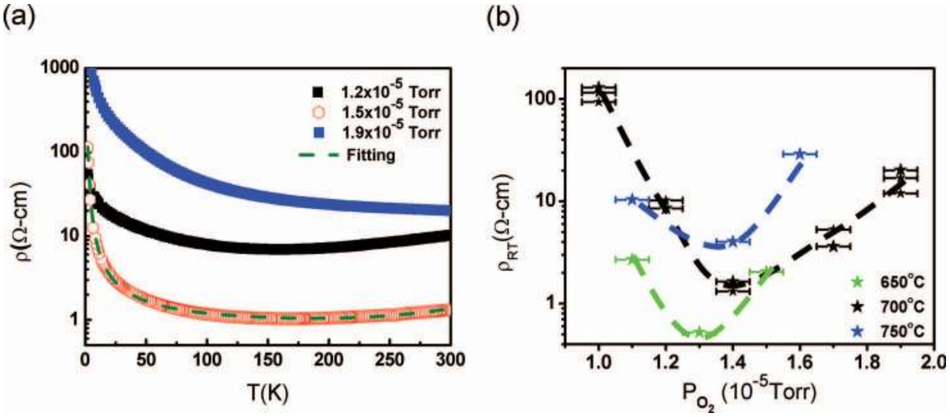

FIG. 1. (a) Temperature dependent measurement of resistivity for samples prepared under deposition temperature 700°C and oxygen partial pressure 1.0×10^{-5} Torr, 1.4×10^{-5} Torr and 1.9×10^{-5} Torr respectively. The green dashed line is the fitting. (b) Statistical study of the resistivity of the samples prepared under different conditions.

lambda Physik pulsed laser ($\lambda = 248$ nm) with energy density of 2 J/cm^2 and a frequency of 5 Hz was used for ablating the target. The base pressure was kept at 5×10^{-7} Torr for all the depositions. Half an hour deposition typically gives 100nm thick films, which was measured by step profiler and also confirmed by Rutherford backscattering (RBS). The crystal structure of the films were examined by X-ray diffraction (XRD) technique using Bruker D8 Discover system (using $\mathrm{Cu}_K = 1.5406$ Å line). The XRD data shows only anatase (004) and (008) peaks for all the measured samples (not shown here). The films were further structurally characterized by RBS and ion channeling by looking at the oxygen surface peak with a 3.04MeV oxygen resonance reaction (8 KeV resonance line width) with 3.04 MeV He^+ ion beam. Hall effect and temperature dependent resistivity (R-T) were obtained by using a physical property measurement system (Quantum Design).

III. RESULTS AND DISCUSSIONS

Temperature dependent resistivity of samples prepared under 700°C and with different oxygen partial pressures were shown in Fig. 1(a). The resistivities of the films for pressures above 10^{-4} Torr are too large to be measured by our system. Surprisingly, a sharp resistivity minimum is seen at a partial pressure 1.4×10^{-5} Torr. For the samples prepared with 650°C and 750°C, the resistivity minimum was located quite close to this pressure as well and the minimum resistivity values shifted with deposition temperatures systematically, as shown in Fig. 1(b). As is well known, oxygen vacancies are donors in $\mathrm{TiO_2}$. Increasing oxygen vacancies should increase the charge carrier densities and the conductivity,[11,12] in disagreement with the present experimental results. To investigate the validity of the results, a statistical study was done, especially for the samples prepared under 700°C. As shown in Fig. 1(b), resistivities of more than ten samples at room temperature were plotted as the function of oxygen partial pressure within a narrow pressure range. Although this data is shown only for room temperature a similar behavior is observed over the whole temperature range. A similar valley was observed in reduced rutile $\mathrm{TiO_2}$ bulk crystal, where the resistivity minimum was correlated to the change in the defect structures.[13] In that system, the charge donor was recognized as Ti interstitials and over reducing the sample led to the formation of planar defects and clustering of the donor defects. The carrier densities of the samples in current system under this preparation condition are well below the Mott limit which is close to 5×10^{18} cm^{-3} (assuming an electron effective mass of 1 and a dielectric constant of 31).[14–16] Hence the electron transport is through hopping and this will depend on the number of carriers and also the number of hopping sites which will be most likely compensating centers arising from cationic defects.[17] In oxides such as $\mathrm{TiO_2}$ it has been observed that oxygen vacancies increase with decreasing pressure and compensating defects increase with increasing oxygen pressure.[18] Hence a cross-over is expected where the highest hopping conductivity will be seen which in this case corresponds to 1.4×10^{-5} Torr. As can be seen in Fig. 1(b), for the

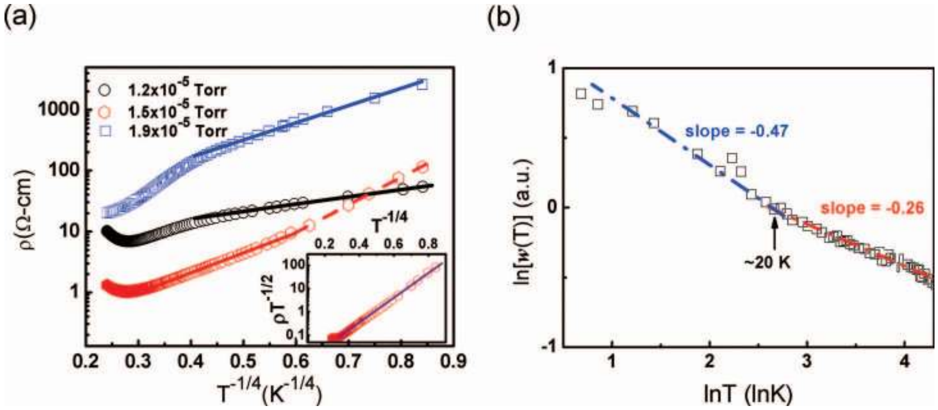

FIG. 2. (a) Plot of resistivity with temperature by Mott VRH theory. Inset is the plot by taking in to consideration the temperature dependent pre-exponential factor. The dashed lines were drawn to guide the eyes. (b) Mathematical approach to distinguish Mott VRH and ES VRH, as described in text. The dash lines are for guiding the eyes.

samples prepared under 700°C, small changes of the oxygen partial pressure can induce huge changes of the resistivity exceeding almost two orders of magnitude over a 50% change in pressure. This may be because the electron hopping probability exponentially depends on the distance between the two hopping sites which is oxygen pressure dependent.[17]

We will now examine the VRH in the three pressure regions depicted in Fig. 1(a). As described by Mott, in deriving the formula for VRH, electrons would tunnel between localized states induced by random potential when and only when compensating levels are involved. Theoretically, random potential would induce localized states near the Fermi level; hence the charge transport will occur among these occupied and empty localized states with the assistance of phonons.[17,19] Mott, assuming a constant density of states (DOS), derived an expression of resistivity as function of temperature as following:

$$\rho = C \cdot \exp\left[\left(\frac{T_0}{T}\right)^{1/4}\right], \text{ where } C \text{ and } T_0 \text{ are constants} \tag{1}$$

By further decreasing the temperature, Efros and Shklovskii (ES) modified the expression by considering the Coulomb correlations between the electrons, which would induce a Coulomb gap in the DOS. The modified expression is not so far from equation (1):

$$\rho = C^* \cdot \exp\left[\left(\frac{T_1}{T}\right)^{1/2}\right], \text{ where } C^* \text{ and } T_1 \text{ are constants.} \tag{2}$$

The pre-exponential factor C and C^* were also investigated as function of temperature theoretically using percolation theory[19,20] though, experimentally it was difficult to justify the existence of the temperature dependent pre-exponential factor.[21]

As shown in Fig. 2(a), the resistivities of the samples were plotted with temperature according to Mott's VRH formula (equation (1)). Equation (1) was satisfied over a large range of temperatures for all three samples in Fig. 1(a), particularly for the sample prepared under 1.4×10^{-5} Torr oxygen partial pressure. The charge transport mechanisms for samples prepared under oxygen partial pressure 1.2×10^{-5} Torr and 1.9×10^{-5} Torr is not fully fitted by VRH. At first glance, the situation of the 1.4×10^{-5} Torr sample should be similar, as we can see the changing of the slope of the straight line indicated by the green dashed line. However, this slope change can be avoided when the temperature dependent pre-exponential factor is taken into consideration,[22] as shown in the inset of Fig. 2(a). An alternative to the temperature dependent pre-exponential factor is the cross over from Mott VRH to ES VRH. Using an approach which treats the pre-exponential factor as constant[23,24] equation (1) and (2) can be combined as

$$\rho = \rho_0 \cdot \exp\left[\left(\frac{T_0}{T}\right)^{v}\right] \tag{3}$$

where, the exponential factor v may separate the Mott VRH from ES VRH. Mathematically, a function w(T) can be built as:

$$w(T) = -\frac{d\ln\rho}{d\ln T} = v\left(\frac{T_0}{T}\right)^{v}. \tag{4}$$

Then the value of v can be obtained by making a linear regression fit to the log [w(T)] versus log T, where the slope of the plot is equal to v. As shown in Fig. 2(b), a changing of v value can be observed, which may indicate a cross over from Mott VRH to ES VRH with further decrease in temperature. The transition temperature is around 20 K. As both the temperature dependent pre-exponential factor and the VRH transition can be used to explain the data, the charge transport mechanisms below 20 K remains an open question.

The metallic part of the resistivity at temperatures above the resistivity minimum can be fitted quite well with the formula considering electron phonon scattering. By taking the following formula, which covers the metallic and insulating range, the resistivity data of the sample prepared under oxygen partial pressure of 1.4×10^{-5} Torr can be fitted well, as shown in Fig. 1(a) by the green dashed line.

$$\rho = A\cdot T^5 + B\cdot T + C\cdot\exp\left[\left(\frac{T_0}{T}\right)^{1/4}\right] + D \tag{5}$$

where A, B, C, D, and T_0 are constants. The metal to insulator transition temperature depends on those constants. Typically, it decreases with the room temperature resistivity of the samples, although there are no obvious reasons behind this.

In many spintronic applications magnetic fields are used. It will thus be important to understand the MR behavior of these VRH insulators. As shown in Fig. 3(a), MR in transverse geometry at 2 K and 5 K is positive; however, it becomes negative when the temperature is above 10 K. In this measurement, *H* // [001], *J* // [010], as shown in Fig. 3(b), *H* is the applied magnetic field, *J* is the current density and [001] is the direction perpendicular to the plane of the sample. Interestingly, at 8 K, the MR is negative at low field and then becomes positive at high field, a result of the superposition of two curves with different signs. The negative MR could be explained by the theory of quantum interference (QI), which occurs between the initial and final states during the hopping paths. This theory has been applied in many other systems in the VRH regime quite successfully.[25,26] The positive MR could be explained by the theory developed by Shklovskii,[19] who considered the shrinkage of the electron wave function in magnetic field, which reduces the overlap between states and hence increase the resistivity. By this theory, at low field (8 T should be low in his theory), the *MR* satisfies following equation:

$$\ln(MR+1) = \gamma H^2 T^{-3/4}, \tag{6}$$

where γ is a constant. As can be seen, the positive *MR* depends on both the magnetic field and the temperature. The relatively large variations of MR from 2 K to 5 K and above are similar to the theoretical precdiction. Of course the scattering of the hopping electrons by impurity centers might participate as well, as suggested by Kitada.[12] Qualitatively, MR induced by QI and shrinkage of the electron wave function both decrease with increasing temperature though the latter has the major influence. This can be used to explain the changing behavior of MR with increasing temperature, which goes from large positive value to large negative value and then approaches zero. Interestingly, all the experimental curves in Fig. 3(a) could be fitted with small error by cubic polynomials, which is a result of the combination of the two mechanisms indicated above.

Angular dependent MR was measured at different fields and temperatures for the film, as shown in Fig. 3(c); they were almost identical whether *H* was rotated in (010) or (100) planes. This is expected as the electron mean free path is far shorter than the film thickness of 100 nm. The MR which was anisotropic could be fitted with a cosine function with the same period, but

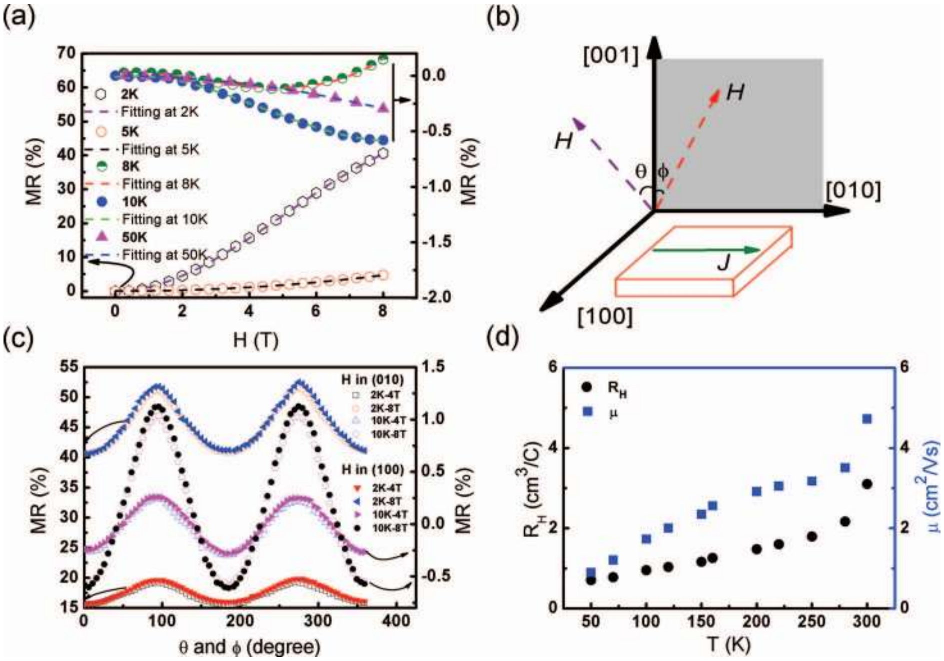

FIG. 3. (a) Transverse MR of the sample prepared under oxygen partial pressure of 1.4×10^{-5} Torr at different measurement temperatures. The arrows indicate the corresponding axis for the data measured at different temperatures. The dashed lines are fit to cubic polynomials. (b) Schematic diagram showing the MR measurement. (c) Angular dependent MR of the same sample under different measurement temperatures and magnetic fields. Rotation angles are described in (b) and the arrows indicate the corresponding axis for the data. (d) Hall coefficient (left axis) and mobility measurement (right axis) above 50 K for the same sample.

different amplitude. The anisotropy is a well known factor induced by quantum interference arising from orbital effect. A similar phenomenon has been observed in other systems, where QI was the dominant mechanism in the VRH regime.[27]

As discussed above, VRH while dominant at low temperatures is involved in the whole measurement temperature range. Hall measurements can unambiguously distinguish between band and hopping transports. The hall mobility μ_H satisfies the following equation:[28,29]

$$\ln \mu_H \propto -\frac{3}{8}\left(\frac{T_0}{T}\right)^{1/4}, \tag{7}$$

where T_0 is the same constant as in equation (1). Although a simple Drude model relating the Hall coefficient R_H and charge carrier mobility is not valid in VRH regime anymore, abnormal R_H plot strongly suggests non-conduction band transport mechanism,[30] as can be seen in Fig. 3(d), where both R_H and μ_H increase with temperature. Qualitatively, the measured μ_H follows this theory but the quantitative discrepancy between experiment and theory probably comes from the large scattering at high temperatures. The Hall measurement below 50 K was difficult to obtain due to enhanced fluctuations in the data.

In summary, we have shown the discovery of an anomalous resistivity minimum in a TiO_2 film prepared at different temperatures and pressures. The resistivity is a very sharp function of oxygen pressure. In most of the pressure range the transport is variable range hopping at low measurement temperatures. Magnetoresistance of the sample prepared at 1.4×10^{-5} Torr was positive at low temperature (for VRH) but negative beyond 10K indicating quantum interference effects further supported by angle dependent MR measurements. Our study emphasizes the importance of paying attention to the preparation condition for TiO_2 layers as insulating barriers in electronic or spintronic devices.

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