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Rectifying Characteristics and Transport Behavior in a Schottky Junction of $CaCu_3Ti_4O_{12}$ and Pt *

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$CaCu_3Ti_4O_{12}$ (CCTO) thin films were fabricated on ITO-covered MgO (100) substrates. The rectification characteristics were observed in the CCTO capacitance structure with Pt top electrodes at temperatures ranging from 150 K to 330 K, which are attributed to the formation of a Schottky junction between n-type semiconducting CCTO and Pt due to the difference of their work functions. At low forward-bias voltage, the current-voltage characteristics of the Schottky junction follow $J = J_{sD}\exp(\frac{qV}{k_0T})$. A strong decrease in ideality factor with the increasing temperature is obtained by linear fitting at the low bias voltage.

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$CaCu_3Ti_4O_{12}$ (CCTO) has attracted great attention in recent years due to its potential applications in devices based on its giant-permittivity properties.[1−5] CCTO material is thought of as an insulator similar to many other perovskite oxides ($CaTiO_3$, $BaTiO_3$). Semiconducting behavior has also been reported in CCTO ceramics by an impedance spectroscopy study.[5] It has been realized that CCTO has n-type conduction by electrons which may result from oxygen vacancies or from the substitution of Ti in the Cu sites.[6] Great efforts have been devoted to the study of its current-voltage characteristics.[7−10] The leakage and semiconducting behaviors have been attributed to semiconducting grains[5] and insulator grain boundaries.[7] However, the origin of leakage current and the conduction mechanism in CCTO have not yet been fully understood, and there are still some debates about the I–V nonlinear behavior of CCTO, especially at the interface of CCTO and metal.

In this study, $CaCu_3Ti_4O_{12}$ (CCTO) thin films were fabricated on ITO-covered MgO (100) substrates. The electrical and transport properties of the CCTO thin films were measured on the capacitance structure of Pt/CCTO/ITO. According to the experimental results, the observed rectifying characteristics are attributed to the formation of a Schottky junction between n-type semiconducting CCTO and Pt due to the difference of their work functions.

CCTO thin films were grown on ITO-covered MgO (100) substrates by pulsed laser deposition (PLD). The beam of a Lambda Physik XeCl excimer laser (308 nm, 20 ns, 4 Hz) was focused on a sintered CCTO or ITO target with an energy density of about 2 J/cm^2. During the deposition process, the substrate temperature was kept at about 780℃ and the oxygen pressure was about 20 Pa. Before the deposition of CCTO, ITO films were fabricated on MgO substrates directly as the bottom electrode. Finally, Pt dots with a diameter of 2 mm were deposited on the CCTO films as the top electrodes. In dots were also fabricated as top electrodes for comparison. The thicknesses of Pt, CCTO and ITO films were determined by a surface profile measuring system (DEKTAK, USA) to be 90 nm, 300 nm and 200 nm, respectively. The crystalline structure of the CCTO film was analyzed by x-ray diffraction (XRD) with Cu Kα radiation at 1.54 Å. The electric properties were measured by a Keithley 2400 sourcemeter.

The XRD pattern of the CCTO thin film on ITO-covered MgO (100) substrate is shown in Fig. 1. Besides the peaks for ITO (222) and (700) reflections, the peaks for CCTO (220) and (310) reflections can be observed clearly, and no impurity peaks are detected. Moreover, the intensity of the (220) peak is much higher than those of other reflections. This can be explained by the lattice mismatch between ITO and CCTO. The lattice constants of CCTO and ITO are 0.739 nm[1] and 1.01 nm,[11] respectively. Thus, the diagonal length in (220) direction of CCTO is 2.09 nm, which perfectly matches with 2.02 nm for the value of two times of the ITO lattice constant. Thus the CCTO film are highly (220) oriented. Figure 2 dis-

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plays the scanning electronic microscopy (SEM) image of the surface of the CCTO film. The cubic grain of the pure CCTO film can be observed clearly due to its body-centred cubic crystal structure.[12]

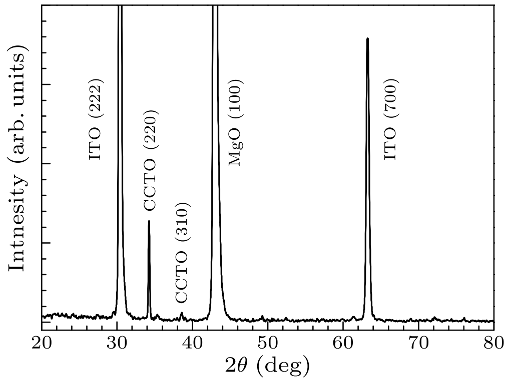

Fig. 1. XRD spectrum of the CCTO film on an ITO covered MgO (100) substrate.

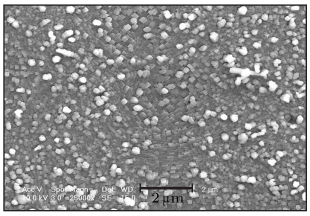

Fig. 2. Scanning electronic microscopy of the CCTO film surface.

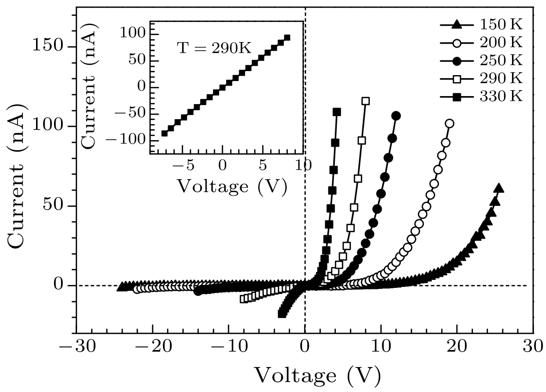

Fig. 3. The I–V characteristics of the ITO/CCTO/Pt junction at different temperatures. The inset shows the I–V relationship of ITO/CCTO/In.

Figure 3 shows the I–V curves of the Pt/CCTO/ITO capacitance structure at different temperatures. Forward bias was defined as a positive pole of dc voltage applied on the Pt top electrode. It can be seen that the I–V behavior demonstrates clear rectifying characteristics. Under forward bias, the current increases very quickly after the voltage exceeds a threshold value. As the temperature decreases, the threshold voltage is enhanced and the current is reduced under the same bias. Under reverse bias, the current is very small and increases slowly with voltage at low temperature, and the reverse current increases obviously with increasing temperature. The inset of Fig. 3 shows the I–V relationship of a sample with In as the top electrode, in which no rectifying behavior was observed.

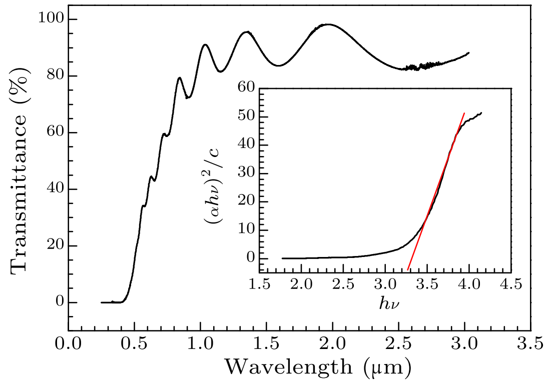

Fig. 4. The linear optical transmittance spectrum of the CCTO film on ITO/MgO. The inset shows the plot of $(h\nu\alpha)^2$ versus $h\nu$ for the film, from which the value of band gap can be calculated.

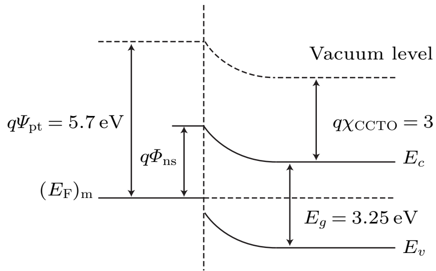

Fig. 5. The band structure of the CCTO/Pt Schottky junction.

To explain the observed I–V behavior, the band structure of the CCTO/Pt junction needs to be analyzed. First, for calculating the band gap of the CCTO film, the linear optical transmittance spectrum of the CCTO film has been measured by using the transmittance spectrum of ITO/MgO as the background, as shown in Fig. 4. The oscillating transmittance indicates that the film has a flat surface and a uniform thickness. The band-gap energy E_g of the CCTO film has been calculated to be about 3.25 eV, slightly larger than the reported value 2.88 eV.[13] The values of electron affinity for CCTO, Pt and ITO [$\chi\,(\mathrm{CCTO}) = 3\,\mathrm{eV}$,[14] $\psi\,(\mathrm{Pt}) = 5.7\,\mathrm{eV}$[14] and $\psi\,(\mathrm{ITO}) = 4.7\,\mathrm{eV}$[15]] are taken to construct the band structure. The concentration of free carriers in CCTO is very low, so the work function of CCTO can be obtained approximately by $\chi\,(\mathrm{CCTO}){+}E_g/2 = 4.6\,\mathrm{eV}$, which is close to the ITO work function of 4.7 eV.[15] Thus there is no energy barrier between the interface of ITO and CCTO, and it can be thought of as an ohmic contact. However, the work function of Pt is 5.7 eV, much larger than the work function of n-type CCTO, so a Schottky contact is formed with an energy barrier q_{ns} at the interface between CCTO and metal Pt. The band structure of CCTO and Pt is constructed as shown in Fig. 5. Under forward bias, the energy barrier will be reduced from the CCTO side and the electrons in the conduction band of CCTO may inject into Pt. This leads to a positive current through the junction at a voltage comparable to the built-in potential. Under reverse bias, the built-in potential increases and gives rise to a larger depletion region, which leads to the increase of the energy barrier, so the reverse current is very small. For comparison, an In top electrode was also fabricated because it has a lower work function than Pt. This sample of In/CCTO/ITO shows a linear conduction behavior indicating ohmic contacts at both the interfaces of In/CCTO and ITO/CCTO. This proves that the observed rectifying conduction behavior in Pt/CCTO/ITO is from the Schottky junction between Pt and CCTO.

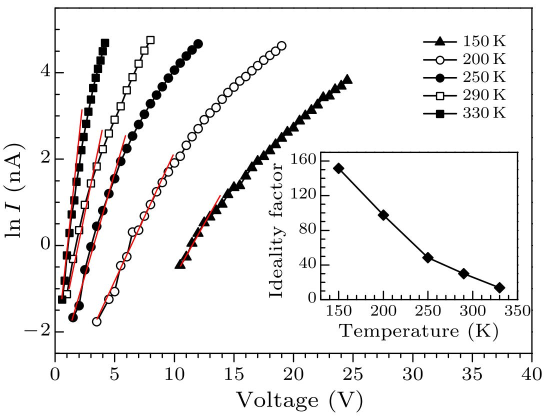

Fig. 6. The $\ln(I)$–V relation under forward bias at different temperatures. The inset shows the relationship between the ideality factor and temperature.

In diffusion theory, the relationship between the current and the applied voltage across a Schottky junction can be expressed as[16]

$$J = J_{sD}[\exp(\frac{qV}{nk_0T}) - 1] \quad \text{for} \quad V \geq 0, \tag{1}$$

$$J = -J_{sD} \quad \text{for} \quad V < 0, \tag{2}$$

where k_0 is the Boltzmann constant, n is the ideality factor, T is the absolute temperature and V is the applied voltage. When $qV \gg k_0T$, which is satisfied in our experiments, Eq. (1) can be simplified to

$$J = J_{sD} \exp\Big(\frac{qV}{nk_0T}\Big). \tag{3}$$

Equation (3) indicates that the junction current increases exponentially with the applied voltage V. Figure 6 shows that $\ln I$ is proportional to V in a low bias voltage range, which is consistent with Eq. (3). As shown in Fig. 6, by linear fitting, the ideality factor can be determined by the slope values. The obtained ideality factor is from 151.6 to 13.6 at a temperature range from 150 K to 300 K, as shown in the inset of Fig. 6. Similar $n-T$ behavior was also observed by Yamamoto *et al.*[17] The ideality factor is defined as[17]

$$\frac{1}{n} \equiv \frac{k_BT}{q}\frac{d(\ln J)}{dV} = 1 - \frac{d\Phi_{ns}}{dV}. \tag{4}$$

The barrier height Φ_{ns} of the Schottky junction depends not only on the electric field in the depletion layers, but also on the bias voltage.[17] As the temperature increases, the carrier concentration in CCTO becomes larger, which will cause a reduction of the value of $d\Phi_{ns}/dV$. Therefore, the value of n decreases with the increase of the temperature.

Moreover, the experimental data deviated from expected values under high voltage. Similar phenomena were also observed in other semiconductor structures.[18] In fact, the model of the Schottky junction is quite simplified and the effect of the interface state is neglected. However, transport behaviors of the carrier at the interface, such as carrier emission, recombination and tunneling, may have a great influence, especially at high voltage.[19] Thus, it is generally observed that the current increases not so quickly as the description of Eq. (3) under high forward voltage bias.

In summary, the rectifying currents at different temperatures have been measured in the Schottky junction of CCTO/Pt. The analysis of the band structure reveals that it is a Schottky contact at the interface of the CCTO and metal Pt, because the work function of Pt is larger than that of n-type CCTO. We explain the I–V behavior in the CCTO/Pt Schottky junction, which would be helpful for understanding the nonlinear I–V behavior in CCTO.

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