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Influence of hopping conduction on the thermopower of indium oxide thick films

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ABSTRACT

We have studied the temperature (T) dependent behaviors of thermopower (S) and resistivity (ρ) of a series of indium oxide (In_2O_3) thick films prepared at different oxygen partial pressures. For the films deposited at lower oxygen partial pressures, the $\rho - T$ curves display metallic characteristics, and the relation between thermopower and temperature is dominated by the electron diffusion process. For the films deposited at higher oxygen partial pressures, the Mott type and Efros-Shklovskii type variable-range-hopping (VRH) processes are observed in the resistivity data. The thermopower obeys $S \propto T^{1/2}$ from ∼50 to ∼200 K, which can be explained by Mott VRH process. At lower temperatures, the existence of phonon-drag causes S to change from negative to positive with decreasing temperature and then present a peak value with further decreasing temperature. Our results demonstrate the validity of theoretical predictions concerning three dimensional Mott VRH thermopower.

1. Introduction

The metal-insulator transition in disordered systems has long been an important physical problem and has been studied intensively [1]. Generally, at low temperatures, the electrical transport properties of weakly disordered systems are determined by the electron-electron interaction and weak localization effects, while the electrical transport properties of strongly disordered systems are governed by the hopping transport. For the hopping transport, the nearest-neighbor-hopping conduction dominates the hopping process at high temperature regime. When the temperature is reduced, the nearest-neighbor-hopping conduction process will be freezed. In this case, the electron will hop from the occupied states to more distant unoccupied states, and the hopping energy is minimum. This is the variable-range-hopping (VRH) conduction process. Considering the density of states (DOS) in the vicinity of the Fermi level is a constant, Mott has suggested that the resistivity ρ obeys $\ln \rho \propto T^{-1/4}$ for the strongly disordered three-dimensional (3D) systems, which is called Mott VRH law [1–3]. Subsequently, Efros and Shklovskii realized the electron-electron Coulomb interaction would open a Coulomb gap and the DOS would tend to zero at Fermi level. The Coulomb gap cannot be ignored at sufficient low temperature, and the temperature behavior of resistivity will obey $\ln \rho \propto T^{-1/2}$, which is called Effos-Shklovskii (ES) VRH law [3–5].

The hopping processes also affect the thermoelectric power (or thermopower, S) of the systems. The VRH thermopower had been investigated by several groups [6–8]. It was found that the electronic DOS in the vicinity of the Fermi level (for the VRH conduction mechanisms) comprises two parts: the symmetric part and the asymmetric part (with respect to Fermi energy). The symmetric part of DOS does not contribute to the thermopower and both the magnitude and the sign of S are determined by the asymmetric part of DOS (even if it is small). In this case, the Mott and ES VRH thermopower, $S_M(T)$ and $S_{ES}(T)$, in three dimensional strongly disordered systems, should obey [6]

$$S_M(T) = -\frac{k_B^2 (T_M T)^{1/2}}{8|e|} a_M, \tag{1}$$

and

$$S_{ES}(T) = -\frac{k_B^2 T_{ES}}{2|e|} a_{ES}, \tag{2}$$

respectively, where k_B is the Boltzmann constant, e is the electron charge, a_M and a_{ES} are the numerical coefficient, T_M is the characteristic temperature of Mott VRH conduction [1–3], and T_{ES} is the characteristic temperature of ES VRH conduction [3–5]. The similar expressions have also been derived by Mott, Burns and Chaikin [2,9]. Experimentally, both the Mott and ES VRH conduction laws (the relation between ρ and T) have been observed in ZnO, In_xO_y, Sr_2IrO_4, $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$,

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Bi, $Cu_6Fe_4Sn_{12}Se_{32}$, and $LaSr_2Mn_2O_7$ [10–17]. However, the predictions of Eqs. (1) and (2) have not been reported in more materials other than $Sr_2Y_{0.5}Ca_{0.5}Co_2O_7$ [13]. Hence the validity of Eqs. (1) and (2) still needs to be further tested.

In the present paper, we systematically investigated the experimental results of thermopower and resistivity as functions of temperature for a series of In_2O_3 films deposited at different oxygen partial pressures. We found a crossover from Mott-type to ES-type VRH conduction processes with decreasing temperature in the resistivity data. Moreover, the relation between thermopower and temperature over the entire Mott VRH conduction regime can be well described by Mott VRH thermopower theory. However, at lower temperatures, S changes from negative to positive, and then reaches a peak value. It is not in agreement with the existing theory of ES VRH thermopower, but these properties of thermopower could be caused by the phonon-drag thermopower. Our results concerning the thermopower and resistivity data are presented and discussed below.

2. Experimental method

In_2O_3 films were deposited on the glass substrates by RF sputtering method. The sputtering source is an In_2O_3 target (99.99% in purity). To obtain In_2O_3 films with different oxygen contents, the deposition was carried out in a mixture of argon and oxygen atmosphere, and a pure Ar gas and a mixture gas of Ar and O_2 (with a volume ratio of 2:98) were added into the mixing chamber. Before sputtering, the base pressure of chamber was below 1×10^{-4} Pa. During deposition, the substrate temperature was fixed to 723 K, the sputtering pressure was 0.55Pa, together with the oxygen partial pressure (volume ratios of O_2 and Ar) in the Ar-O_2 mixture gas was set to 0%, 0.12%, 0.9%, 1%, and 2%, respectively. The thicknesses and structures of films were measured by a surface profiler (DEKTAK, 6M) and a Rigaku x-ray diffractometer (D/max-2500v/pc) with CuK_α radiation, respectively. Table 1 lists the values of thicknesses. The four-probe Hall effect and thermoelectric power measurements were performed on a physical property measurement system (PPMS-6000, Quantum Design). The resistivity were also measured by the four-probe method, in which a Keithley 236 outputs current and a Keithley 2182 A measures voltage.

3. Results and discussions

Fig. 1 shows the XRD patterns for three representative samples, as indicated. The position and intensity of the diffraction peaks are similar to those of the powder In_2O_3 samples, eg. the powder diffraction file No. 06-0416 (cubic structure). This indicates that our samples are polycrystalline films. From the six diffraction peaks indexed in Fig. 1, we obtained the mean values of the lattice constant of the films and listed them in Table 1. Inspection of Table 1 indicates that the lattice constant decreases with increasing oxygen partial pressure. Generally speaking, oxygen vacancies are prevailing and act as donor-doping in In_2O_3 films [18–25]. Under O-rich condition, indium vacancy, acting as deep acceptor, has the lowest formation energy [26,27]. On the other hand, both oxygen vacancies and indium vacancies could result in

Table 1
Sample parameters for the five In_2O_3 films. O_{pp} is the oxygen partial pressure, t is the mean film thickness, ρ (300 K) is the room temperature resistivity, and n (300 K) is the room temperature carrier concentration obtained from Hall effect measurements. The values of a is the lattice constants obtained from XRD.

Film	O_{pp} (%)	t (μm)	ρ (300 K) (mΩ cm)	n (300 K) (10^{18} cm^{-3})	a (Å)
1	0	1.05	2.67	47.91	10.1432
2	0.12	1.44	38.01	38.31	10.1394
3	0.9	1.29	1822.0	1.35	10.1321
4	1	1.19	2509.4	0.69	10.1344
5	2	1.12	5652.1	0.32	10.1297

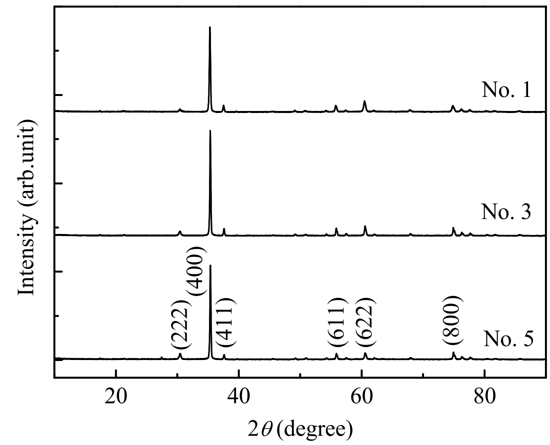

Fig. 1. Typical $\theta - 2\theta$ x-ray diffraction patterns for three representative samples, as indicated.

shrink in lattice constant of In_2O_3 [28]. Therefore, the reduction of lattice constant in In_2O_3 could originate from the enhancement of the concentration of indium vacancies with increasing oxygen partial pressure.

Fig. 2(a)–(c) show the temperature dependence of resistivity for films Nos. 1-5. The temperature coefficient of resistivity for film No. 1 is positive above ~180 K and is negative below ~180 K, while they are negative in the whole measured temperature range for films Nos. 2-5. Hence, film No. 1 possesses metallic transport properties. The logarithmic derivative $d \ln \sigma / d \ln T$ of the conductivity σ is more sensitive than the temperature coefficient of conductivity [29]. According to this more accurate criterion, the $d \ln \sigma / d \ln T$ of metallic samples tends to zero, nevertheless, the $d \ln \sigma / d \ln T$ of insulating samples tends to infinity or constant as T approaches zero. We used this more accurate criterion to distinguish between metallic and insulating behaviors. The inset of Fig. 2(b) and (c) present $d \ln \sigma / d \ln T$ as a function of $T^{0.5}$ for films No. 2 and No. 3, respectively. Clearly, the $d \ln \sigma / d \ln T$ tends to zero and infinity for films No. 2 and No. 3 (films No. 4 and No. 5 also possess the same characteristic with film No. 3), respectively, as T approaches zero, indicating that film No. 2 and films Nos. 3-5 present metallic properties and insulating properties in electrical transport, respectively [29,30].

In three-dimensional systems, the resistivities of Mott-VRH and ES-VRH conducting processes can be written as [1–5]

$$\rho = \rho_M \exp\,(T_M/T)^{1/4}, \tag{3}$$

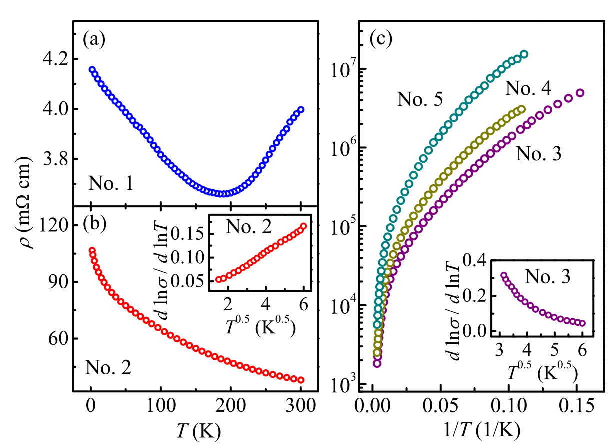

Fig. 2. (a)-(b) Resistivity versus temperature for the two least resistive films, as indicated. (c) The logarithm of resistivity versus T^{-1} for the three most resistive films, as indicated. The insets of (b) and (c) show $d \ln \sigma / d \ln T$ versus $T^{0.5}$ for films No. 2 and No. 3, respectively.