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Metal-semiconductor transition and negative magneto-resistance in degenerate ultrathin tin oxide films

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ABSTRACT

A study of electron- and magneto-transport behavior of ultrathin SnO_2 films of thickness ≤40 nm with high conductivity of 537 Ω^{-1} cm^{-1} deposited on glass substrate by using DC reactive sputtering has been carried out at low temperature. Hall effect measurements revealed these SnO_2 films to be degenerate down to 40 K. The films with thickness >5 nm are found to undergo a metal-semiconductor transition below 140 K, and show a negative MR of ~1.5% at a magnetic field of 0.9 T below 40 K. Both these phenomena have been ascribed to the presence of weak localization of electrons at low temperature. Electron transport behavior has been explained using quantum correction to conductivity. Estimated inelastic scattering lengths were found to be longer than the film thickness which supports two-dimensional nature of electron- and magneto-transport in these ultrathin films.

1. Introduction

The remarkable optical (high UV–visible transparency) and electrical (resistivity down to 10^{-3} Ω cm) properties of SnO_2 thin films allow for numerous applications as passive (transparent conducting electrodes, sensors, photocatalysts, etc.) [1] and active devices (UV light-emitting diodes (LED), white light LEDs or thin film transistors) [2–4]. Efforts have been made to improve/tailor physical properties of SnO_2 thin films for their specific applications and to understand various phenomena including electron transport [2–5]. It is well known that the as-deposited SnO_2 films generally suffer from donor-type defects such as tin interstitials (Sn_i), and oxygen vacancies (V_O) which are responsible for the disorder in this system and contribute conduction electrons that cause high electrical conductivity [6]. At low temperatures the scattered electron waves produce the constructive interference effect, which is known as weak localization (WL) effect [7]. Because of this weak localization of electrons, the resistivity ρ varies as $\rho \propto -T^{1/2}$ in disordered three-dimensional (3-D) systems and as $\rho \propto -lnT$ in two-dimensional (2-D) systems [7]. These theoretical predictions of WL have experimentally been confirmed in many semiconducting as well as metallic thin films [8,9].

The electrical properties of pure and doped SnO_2 thin films of thickness >100 nm have been investigated by several groups. It has been found that the SnO_2 films doped with different elements (F, Sb, and Ta etc.) exhibit a metallic conductivity at room temperature followed by a metal-semiconductor (MS) transition at lower temperatures [10–12]. On the contrary, undoped SnO_2 thin films were found to show the classical semiconducting behavior [13,14] at thicknesses above and below 100 nm. The magneto-transport properties of non-magnetic SnO_2 thin films have so far been reported by two groups [11,15]. In one case the observed negative magneto resistance (−MR) of 0.8% at 2–8 K in 200 nm thick undoped non-degenerate SnO_2 films was ascribed to a 2-D like electron transport [15] while in the other case of 650 nm F-doped SnO_2 films a −MR at 12–36 K is attributed to 3-D like electron transport [11].

In this work we have investigated the temperature dependent electron- and magneto-transport properties of the undoped ultrathin SnO_2 films with thicknesses in the range of 5–40 nm. Films of high conductivity of 537 Ω^{-1} cm^{-1} have been obtained by pulsed-dc magnetron reactive sputtering technique [16]. The presence of a metal-like conduction behavior near room temperature and an MS transition at ~140 K is observed in our ultrathin films. Also a −MR is observed in these ultrathin SnO_2 films at temperatures 18–40 K. The unusual metallic conductivity of undoped ultrathin tin oxide films, the MS transition and the −MR are interpreted in the frame

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work of quantum corrections to conductivity in the degenerate ultrathin tin oxide films.

2. Experimental detail

Ultrathin nanocrystalline SnO_2 films each with a thickness of 5, 10, 20 and 40 nm were deposited on glass substrate, by pulsed dc reactive magnetron sputtering technique [16]. Films of thickness 70 and 110 nm were also deposited for comparative study. The films are almost atomically flat with a surface roughness of ~1 unit cell of SnO_2. The X-ray diffractograms of the ultrathin films were recorded in grazing angle mode ($\theta = 0.5^\circ$) by using Cu Kα radiation ($\lambda = 1.5406$ Å). The carrier concentration (n) of these films was estimated using Hall measurements at room temperature as well as at low temperature. The electrical resistivity measurements were carried out using van der Pauw method in the temperature range of 300–18 K. The magnetic field dependence of resistance was investigated in the temperature range of 18–40 K. An external dc magnetic field (up to 1 T) was applied perpendicular to the film surface.

3. Results and discussion

The XRD patterns of the ultrathin SnO_2 films are shown in Fig. 1. We observe a very weak peak located at 51.9° that corresponds to (211) plane of SnO_2 tetragonal phase [JCPDS-411445]. This peak slightly grows in intensity with film thickness increasing from 10 to 40 nm. However, it is not detected in case of 5 nm thick film. In XRD patterns of 20 and 40 nm thick films two additional very weak peaks corresponding to (110) and (200) planes appear. So from these diffraction patterns it seems that the films are nanocrystalline in nature.

3.1. Electron transport behavior

Fig. 2 shows the resistivity vs. temperature curves for SnO_2 films of different thicknesses in the temperature range of 18–300 K. It could be seen that the electrical transport behavior is significantly affected by the film thickness. For the 5 nm thick SnO_2 film, the resistivity increases with decreasing the temperature from 300 to 18 K, showing a semiconductor behavior (in the entire temperature range) which can be understood in terms of thermally activated

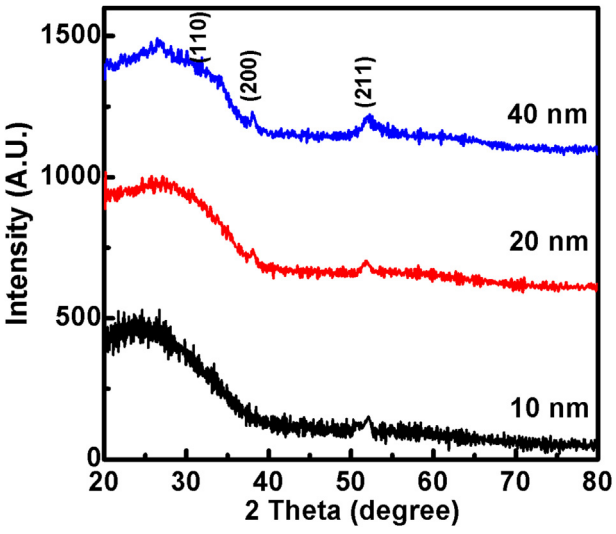

Fig. 1. X-ray diffraction patterns of SnO_2 films of different thicknesses.

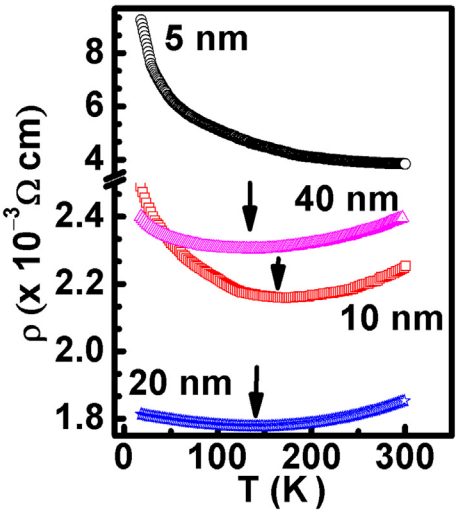

Fig. 2. Variation of electrical resistivity (ρ) vs temperature (T) for SnO_2 films of different thicknesses. Arrows indicate MS transition temperatures that are ~130 K for 40 nm film, ~140 K for 20 nm film and ~165 K for 10 nm film.

transport of electrons. The ρ (T) data of 5 nm SnO_2 was well fitted with Arrhenius equation in the temperature range of 200 K–300 K (Fig. 3(a)); and the thermal activation energy was found to be 4.13 meV. The resistivity data (Fig. 3(b)) follows log ρ vs. $(1/T)^{1/3}$ in the low temperature range of 18–100 K; and the conduction mechanism is thus found to obey Mott variable range hopping (VRH).

It may be noted from Fig. 3 that thicker films (>5 nm) show metallic behavior in conduction in 300–150 K and there occurs a metal-semiconductor (MS) transition in these thicker films as temperature is lowered. This type of temperature dependence of resistance, exhibiting MS transition, has not been reported yet in the case of undoped ultrathin SnO_2 films having thickness 10–50 nm. However, similar temperature – resistance behavior has been observed in case of F doped SnO_2 [11] and Ta doped SnO_2 films [12] having thickness >100 nm. The increase in resistance with decrease in temperature below the transition temperature T_{MS} indicates the localization of electrons [7] whereas increase in resistance with increase in temperature above transition temperature results from delocalized electrons and is a characteristic feature of a degenerate semiconductor. This delocalization of electrons leads to metallic conductivity, which is due to formation of degenerate band with the Fermi level shifting into conduction band. The electronic conduction in degenerate thin films of SnO_2 showing MS transition can thus be explained by a combination of both carrier scattering and activation. The resistivity is given by $\rho = 1/ne\mu$, where e is electronic charge, n is carrier concentration and μ is the mobility. Thus the least value of resistivity observed for 20 nm film is consistent with the maximum values of n and μ found for this thickness value. A minimum resistivity of 1.77×10^{-3} Ω cm is obtained at T_{MS} for the 20 nm film. The explanation for larger values of these to electronic transport parameters is given in our earlier report [16].

The values of transition temperature, T_{MS} were determined using derivative of ρ (T) data. We observe an increase in the T_{MS} value from ~130 K to ~165 K as film thickness decreases from 40 to 10 nm. The variation of T_{MS} value with thickness does not seem to follow the variations of n and μ with thickness. It can be related to electron localization effects. The width of the impurity or defect band in which free carrier exit relates to the electron wave function spread (Bohr radius). This spread decreases with decrease in temperature