Bull. Mater. Sci., Vol. 32, No. 3, June 2009, pp. 227–230. © Indian Academy of Sciences.

Metal–semiconductor nanojunctions and their rectification characteristics

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Abstract. Junctions of silver–copper oxide and silver–zinc oxide, respectively were prepared within the pores of diameters, 20 nm, in anodic aluminium oxide membranes. Voltage–current characteristics were measured over the temperature range 373–573 K which showed rectification behaviour. Using the standard equation the difference between the work functions of the metal and the semiconductor was calculated. This showed a variation with the temperature of measurement. This is explained as arising due to the effect of pressure generated as a result of thermal expansion of the metallic phases concerned between the electrodes. This is consistent with the theoretical prediction of Fermi level shifting of the semiconductor within the bandgap as a function of pressure.

Keywords. Metal–semiconductor nanojunctions; rectification characteristics; nanostructure systems; single-walled carbon nanotubes.

1. Introduction

In recent years there have been a lot of research efforts in the miniaturization of electronic devices using nanostructured systems (Bachtold *et al* 2001; Martel *et al* 2001; Anantram and Léonard 2006). Single-walled carbon nanotubes have been exploited to fabricate field effect transistor (Tans *et al* 1998; Heinze *et al* 2002; Appenzeller *et al* 2002; Javey *et al* 2003). Theoretical analyses show that metal–carbon nanotube contacts and the Schottky barrier formation play a crucial role in the device performance (Zhu and Kaxiras 2006). Metal–semiconductor (oxide) contacts have been investigated but the performance has been shown to be dependent on the pretreatment of the surfaces concerned (Coppa *et al* 2003; Ip *et al* 2004; Kim *et al* 2005; Mosbacker *et al* 2005). Effect of pressure on the Schottky barrier at the metal–carbon nanotube contact has been investigated theoretically (Park *et al* 2005). A shift of the Fermi level within the bandgap of the carbon nanotube has been shown to occur. In the present investigation metal–oxide (semiconductor) nanojunctions have been fabricated by an electrochemical method. No special treatment of the nanojunction was necessary. The voltage–current characteristics have been studied as a function of temperature. An ideal rectification characteristic was obtained. The behaviour could be explained on the basis of a shift in the Fermi level of the nanolayer of the oxide semiconductor as a result of pressure generated by thermal expansion mismatch of the two phases. The details are reported in this paper.

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Dedicated to Prof. C N R Rao

2. Experimental

Figure 1 shows schematically the experimental arrangement for growing the metal–semiconducting oxide nanojunctions. Nanoporous anodic aluminium oxide membranes with thickness, 60 μm, supplied by M/s Whatman (Singapore) were used as templates. The membranes had a pore diameter of 20 nm and a pore density of 10^{10} cm^{-2}. One side of the membrane was vacuum coated with gold. The latter was used as the cathode for the electrochemical growth process. We have prepared Ag–Cu_2O and Ag–ZnO nanojunctions, respectively by the following procedure. For the former as a first step copper nanowires were grown. A copper plate was used as the anode and the electrolyte was a solution of copper nitrate. A preliminary experiment showed that copper nanowires were formed

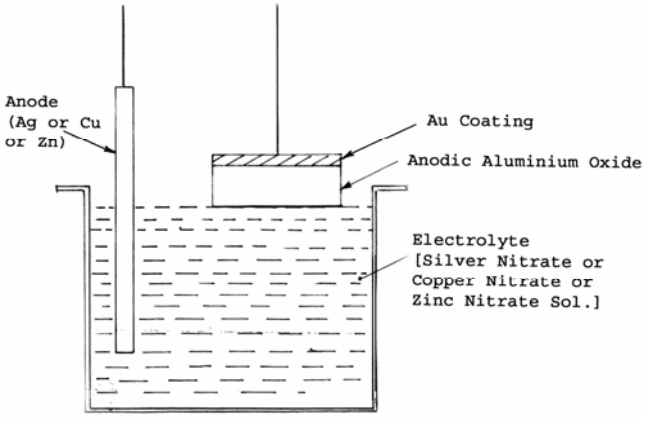

Figure 1. Schematic diagram of experimental arrangement for growing metal–semiconductor oxide nanojunction.

spanning the anode and the cathode by the application of a voltage of 0·16 V for a duration of 4 min. In the present case, 0·16 V was applied for a period of 2 min so that copper nanowires formed covering only a fraction of the pore lengths. This membrane was then kept touching a silver nitrate solution taking a silver rod as anode. Silver nanowires were grown by applying 1 V across the two electrodes for a duration of 3 min. The template was rinsed in alcohol and dried. The latter was subjected to an oxidation treatment at 673 K for 1 h. Copper was oxidized. It is known that Ag_2O dissociates into metallic silver and oxygen at temperature above 500 K (West 1990). Hence by the above process a junction between metallic silver and copper oxide was formed. For preparation of Ag–ZnO nanojunction a zinc rod was used as the anode and zinc nitrate solution as the electrolyte. Zinc nanowires were deposited by the application of 0·8 V across the assembly for a duration of 2 min. After this the rest of the nanopores was filled up by growing silver nanowire following the procedure described above. After rinsing and drying the template with the nanowire assembly the latter was subjected to an oxidation treatment at 673 K for 30 min. Zinc wire was oxidized to ZnO and Ag_2O formed got dissociated into metallic silver and oxygen for reason explained before. Ag–ZnO nanojunctions resulted in the process.

Microstructural studies of the junctions were carried out using JEOL 2010 Transmission Electron Microscope. Voltage–current characteristics for the nanojunctions were delineated using a Keithley 617 Electrometer in the temperature range 370–573 K.

3. Results and discussion

Figure 2(a) shows a transmission electron micrograph for a silver–zinc oxide nanojunction. It can be seen that the diameter of the nanowire is 20 nm which is consistent with the specification of the supplier for the membranes used in the present experiments. The portion of the nanowire which is darker than the rest evidently represents silver metal, the other portion comprising zinc oxide. Figure 2(b) shows the electron diffraction pattern of figure 2(a). The diffraction rings were analysed and the interplanar spacings were calculated. Similar micrograph was obtained for silver–copper oxide nanojunction also. Table 1 summarizes the values of interplanar spacings obtained for both the junctions. It is seen that the junctions in the two specimen systems comprise of Ag–Cu_2O and Ag–ZnO, respectively.

Figures 3(a) and (b) show the voltage–current characteristics for the Ag–Cu_2O and Ag–ZnO nanojunctions, respectively. The nature of the curves imply the rectification characteristics of a metal–semiconductor junction.

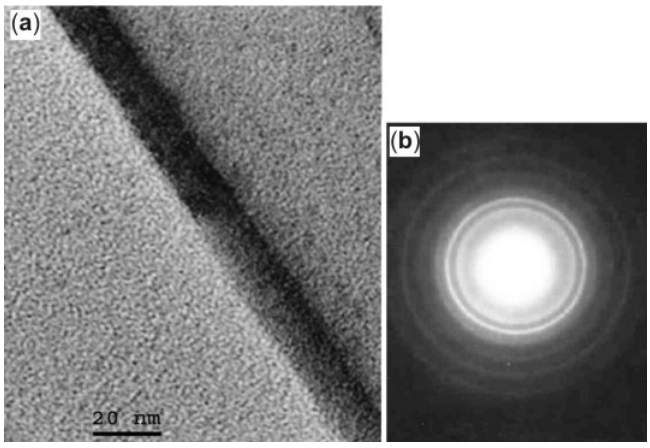

Figure 2. (**a**) Transmission electron micrograph for silver–zinc oxide nanojunction and (**b**) electron diffraction pattern of figure (**a**).

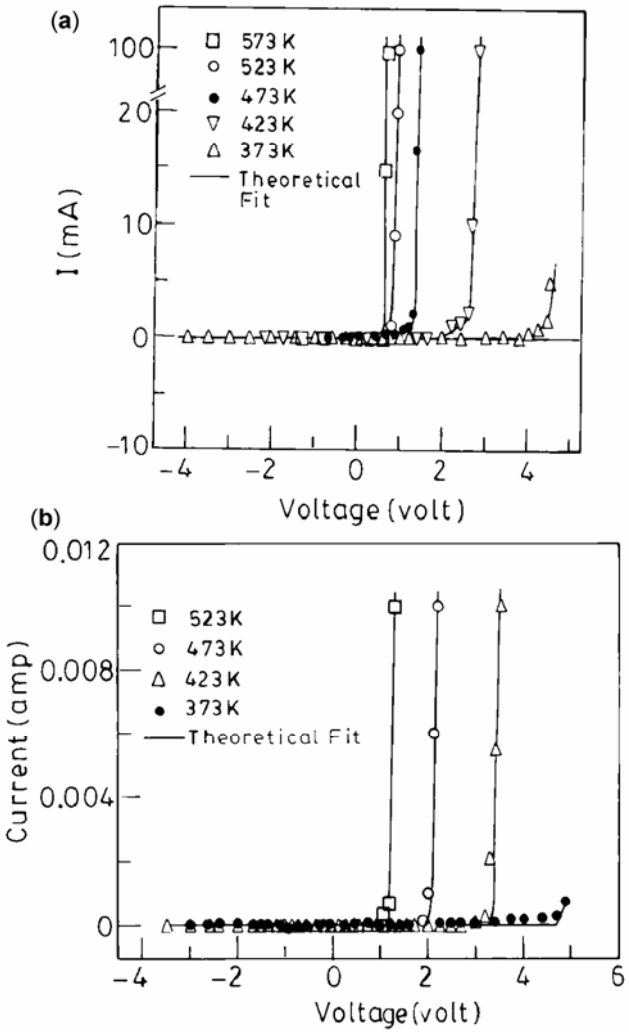

Figure 3. (**a**) Voltage–current characteristics for Ag–Cu_2O nanojunctions and (**b**) voltage–current characteristics for Ag–ZnO nanojunctions.

Table 1. Comparison of interplanar spacings obtained from electron diffraction patterns of the two junctions with ASTM values.

Junction	Observed values, d_{hkl} (nm)	ASTM values (nm)		
		Ag	Cu_2O	ZnO
Ag–Cu_2O	0·288		0·2978	
	0·241		0·2427	
	0·2073	0·200	0·212	
	0·146	0·1443	0·1486	
	0·1235	0·117	0·1274	
Ag–ZnO	0·289			0·281
	0·247			0·24759
	0·226	0·223		
	0·171			0·162
	0·151	0·1443		0·1477
	0·129			0·1301

Table 2. Extracted parameters I_0 and ϕ_0 obtained by fitting experimental V–I data.

Junction	Temperature (K)	I_0 (amp/K^2)	ϕ_0 (eV)	Thermal stress at junction (GPa)
Ag–Cu_2O	373	$5{\cdot}4 \times 10^{-41}$	1·80	0·3
	423	$1{\cdot}3 \times 10^{-21}$	1·57	0·4
	473	$3{\cdot}3 \times 10^{-16}$	0·54	0·6
	523	$5{\cdot}7 \times 10^{-13}$	0·35	0·7
	573	$7{\cdot}4 \times 10^{-11}$	0·22	0·8
Ag–ZnO	373	$4{\cdot}3 \times 10^{-47}$	0·96	0·3
	423	$2{\cdot}1 \times 10^{-32}$	0·98	0·5
	473	$3{\cdot}1 \times 10^{-24}$	0·68	0·7
	523	$9{\cdot}2 \times 10^{-17}$	0·40	0·9

We have fitted the data to the corresponding equation given by Azaroff and Brophy (1963)

$$I = I_0 T^2 \exp\left(\frac{-\phi_0}{kT}\right)\left[\exp\left(\frac{eV}{kT}\right) - 1\right], \quad (1)$$

where I_0 is a constant, T the temperature, e the electronic charge, ϕ_0 the difference between the work functions of the metal and the semiconductor, k the Boltzmann constant and V the applied voltage. The theoretically fitted curves are shown in figures 3(a) and (b). The extracted values of I_0 and ϕ_0 at different temperatures are summarized in table 2. The parameters show a marked variation with temperature which is rather unusual. This is ascribed to the effect of pressure generated at the junction as explained below.

The nanojunctions prepared here comprise of a nanowire of silver and a nanowire of copper or zinc coated with an oxide layer. As the temperature is raised the two portions will expand and because of silver coatings on both the surfaces, exert a pressure at the junction. We have estimated the value of pressure by considering the thermal expansion coefficients of silver, copper and zinc as $17{\cdot}0 \times 10^{-6}$/K, $14{\cdot}1 \times 10^{-6}$/K and $26{\cdot}3 \times 10^{-6}$/K, respectively (Hodgman 1962). Taking the values of Young's modulus for silver, copper and zinc as $7{\cdot}7 \times 10^{11}$ dynes/cm^2, 12×10^{11} dynes/cm^2 and $7{\cdot}8 \times 10^{11}$ dynes/cm^2, respectively (Hodgman 1962), we have calculated the stresses generated at the junctions at different temperatures. The values are in the range of 0·3–0·9 GPa and are summarized in the last column of table 2.

The value of ϕ_0 as shown in table 2 corresponds to the difference between the work functions of the two phases making up the junction. It has been shown by recent calculations (Park *et al* 2005) that this value is dependent on the position of the Fermi levels with respect to the bandgap in the semiconductor. The Fermi level is shifted to either the conduction edge or the valence edge of the semiconductor. Cu_2O has been shown to be a *p*-type semiconductor and ZnO an *n*-type semiconductor (Kingery 1967). In the present case, an increase in pressure will cause the Fermi level in the semiconducting phase to shift either away from the valence edge (Ag–Cu_2O) or away from the conduction edge (Ag–ZnO), thereby causing a reduction in the value of ϕ_0. This is borne out by the results obtained and shown in table 2.

In summary, nanojunctions of Ag–Cu_2O and Ag–ZnO have been produced by electrodeposition followed by

oxidation within anodic aluminium oxide membranes having pores with diameter, 20 nm. Voltage–current characteristics have been delineated over the temperature range 373–573 K. These show rectification behaviour. The parameters extracted by fitting the data to the relevant equation show a variation in the difference of work function between the metal and the semiconductor as a function of temperature. This is ascribed to the effect of pressure generated due to thermal expansion of the metallic phases concerned between the electrodes. This is consistent with the theoretical prediction of the shifting of the Fermi level of the semiconductor within the bandgap as the pressure is increased.

Acknowledgements

The work has been supported by CSIR, Govt. of India, New Delhi. One of the authors (DC) thanks the Indian National Science Academy for the award of an Honorary Scientist position. The authors thank Bhola Nath Pal and Shantanu Bhattacharya for their help. Part of the work was supported by DST, Govt. of India, New Delhi, under its Nano Science and Technology Initiative Programme.

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