Electronic conductivity of mechanochemically synthesized nanocrystalline $Ag_{1-x}Cu_xI$ system using DC polarization technique[*]

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Abstract. A study of electronic conductivity using the DC polarization technique has been carried out for AgI and $Ag_{1-x}Cu_xI$ (where $x = 0.05$, 0.15, 0.25) solid solutions over a range of temperatures from 300 K to 473 K. A diode-like current–voltage characteristics arises from microscopic p-n junctions and an enhanced electronic conductivity of the order of 10^{-3}A is observed for undoped AgI and Cu-doped AgI. Activation energies (E_a) for electronic conductivity obtained from $\log \sigma$ (Ω^{-1} cm^{-1}) vs. $1000/T$ (K^{-1}) were 0.48, 0.6, 0.74 and 1.01 eV for AgI, $Ag_{0.95}Cu_{0.05}I$, $Ag_{0.85}Cu_{0.15}I$ and $Ag_{0.75}Cu_{0.25}I$ solid solutions respectively. The near-twofold increase in activation energy (1.01 eV) observed upon 25% Cu doping is due to the substantial concentration of current carriers/holes injected by Cu while replacing Ag^+ in AgI.

Keywords. Superionic conducting nanomaterials; AgI–CuI solid solutions; electronic conductivity; structural phase transitions.

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1. Introduction

Nanostructured materials have attracted considerable attention in recent years because of the interesting physical properties they exhibit. In the nanofabrication of devices, a diode consists of an addition of micro p-n junctions to be done at low temperature by connecting a series of metal–semiconductor devices whose switching properties is important in recent years. A number of studies were reported on switching in discontinuous metal films and metal–ceramic composites (cermets). In

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the former, electrical conduction was explained as arising due to electrons traveling from one end to another via impurity levels of the substrate surface with electrons emitted into a vacuum (Fowler–Nordheim tunneling mechanism) [1]. Metallic aluminum embedded in aluminum oxide showed metallic property and then switching at a threshold voltage of 0.5 V to a high resistance state. A memory effect was also observed [2]. Dan *et al* have grown one-dimensional arrays of nanometal particles within a silicate glass by an electrodeposition process and found that the nanocomposites exhibit a diode-like behavior at low temperatures in the case of Ag nanocomposites [3]. We have realized that the interface between two nanosemiconductors – one an n-type and the other a p-type – could offer the possibility of acting as nanodiodes while those between a nanometal and a nanosemiconductor could yield a Schottky barrier. With this conjecture in mind, we have investigated the electronic conductivity of a series of solid solutions between AgI and CuI, the results of which are reported in this paper.

In our earlier work, AgI–CuI nanocrystalline materials with crystallite size ranging from 46 to 31 nm prepared by mechanochemical reaction (MCR) were studied for their structure, phase stability and phase transitions with Cu concentration [4]. Later we studied intrinsic paramagnetic defects such as Ag^{2+} (hole center) and Ag^0 (electron center from Ag metal nanoparticles) and probed the superionic phase transition in AgI nanocrystals [5]. Here we report diode-like current–voltage behavior and an enhanced electronic conductivity in undoped AgI and $Ag_{1-x}Cu_xI$ ($x = 0.05$, 0.15 and 0.25) nanocrystalline materials. This drastic effect is attributed to (a) crystallite size reduction, (b) lattice contraction/lattice defect formation and (c) increase in the density of clean/fresh surfaces generated by mechanochemical reaction. AgI is a well-studied superionic conducting material with zinc blende structure at room temperature, and high ionic conductivity [6]. The structures of wurtzite (β-AgI) and zinc blende (γ-AgI) exist below 146.5°C and above this temperature α-AgI (bcc) dominates which is a high temperature superionic phase. AgI is an n-type semiconductor which is purely ionic after the phase transition while CuI is a mixed ionic–electronic conductor at room temperature with predominant electron–hole conduction up to 200°C. The process of MCR introduces a number of steps in the formation of solid solutions; the important one being charged interface formation. These interfaces probably act as microscopic p-n junctions which eventually produce a non-negligible concentration of electronic current carriers in the MCR-derived nanocrystalline powder.

2. Experimental techniques

Compositions corresponding to AgI, Ag-rich $Ag_{1-x}Cu_xI$ where $x = 0.05$, i.e., 5%, 0.15, 0.25 were synthesized by mechanical grinding in a $6''$ agate mortar and pestle for 5 h at room temperature in an unilluminated room using appropriate quantities (in wt%) of copper (LOBA, India), silver (Special Materials Project, Hyderabad, India) and I (Rasayana Laboratory, India). Pellets with dimensions $A \times L = 0.4$ $cm^2 \times 0.2$ cm (area × thickness) were prepared from MCR-synthesized samples under a pressure of 4 tones/cm^2 in a stainless steel die. Pellets were annealed at 373 K (±1 K) in an oven for 3 h followed by cleaning the surfaces with acetone. Crystal
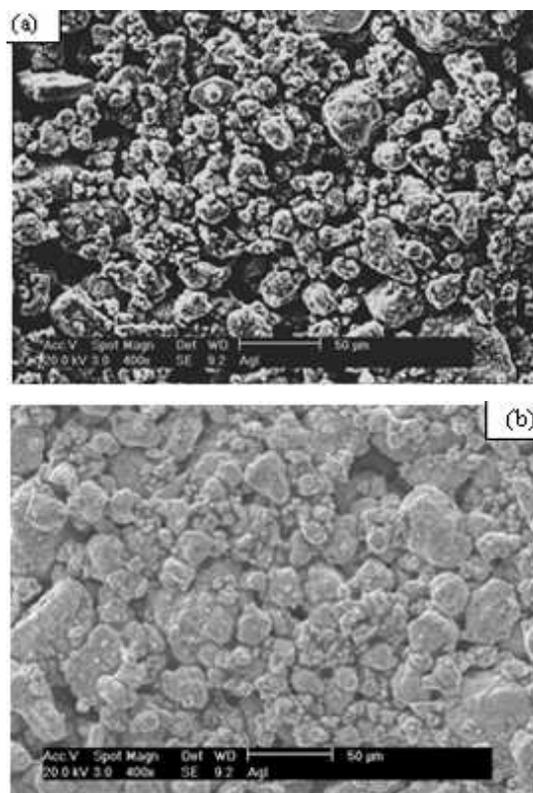
structure and microstructure of undoped AgI have been studied by using Phillips X-ray diffractometer and Phillips XL-30 Series Scanning Electron Microscope respectively. In order to measure the electronic conductivity, graphite and silver electrodes were made with the same dimensions which act as blocking and non-blocking electrodes respectively. The electrode configuration in this case is M/MX/B where M=Ag, MX=(Ag, Cu)I, B=graphite. For the DC polarization technique, measurements were done at 10^{-2} Torr inside an apparatus, which is the same as the one described earlier by Kiukkola and Wagner [7]. A disk-shaped specimen sandwiched between a silver cathode and a graphite anode was mounted and operated based on a spring contact which was supported by long stainless steel rods. Various stable DC potentials were applied and currents corresponding to steady state were recorded using a Keithley digital multimeter 195A connected in series with the specimen. A chromo-alumel thermocouple close to the specimen recorded the temperature which was controlled through an on–off temperature controller unit. The accuracy in the temperature measurements was ±0.5 K. *I–V* characteristics have been done for all compositions.

3. Results and discussion

Figure 1a shows the X-ray diffractogram of MCR-synthesized undoped AgI confirming the formation of zinc blende structure (γ-AgI) as indicated by (1 1 1), (2 2 0) and (3 1 1) peaks. A minor (3%) wurtzite phase (β-AgI) is observed at $2\theta = 22.68°$
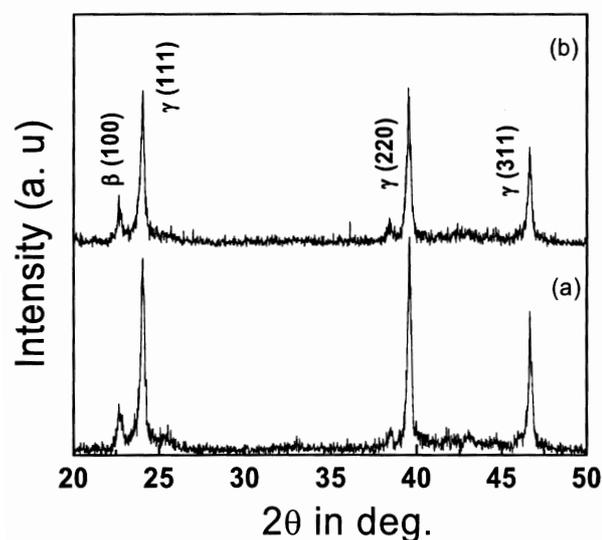
Figure 1. (a) X-ray diffractograms of mechanochemically ground AgI nanoparticles show predominantly zinc blende (γ) structure at room temperature. (b) No qualitative changes are observed after heat treatment at $50°$C for 3 h.

Figure 2. Scanning electron micrographs show the microstructure (morphology) of MCR-synthesized undoped AgI at room temperature (**a**) before annealing and (**b**) after annealing at 50°C.

as indicated by the (1 0 0) peak. In our earlier report on Cu-substituted AgI, we found that the β-phase was totally absent [4]. All MCR samples were pelletized and annealed at 50°C for 3 h before performing electrical measurements. To look for any effects induced by annealing, the annealed samples were characterized by XRD. From figure 1b, it is observed that upon annealing there are no qualitative changes in the structure except for a slight variation in the intensities of the peaks. Similarly we studied the microstructure of undoped AgI by SEM which reveals that there are no significant changes observed after heat treatment. The shape and size of the crystallites were intact in both the cases as seen from figures 2a,b.

In a DC two-probe polarization cell [8,9] of type, $(-)\text{Ag}|\text{Ag}_{1-x}\text{Cu}_x\text{I}|\text{C}(+)$, when a DC potential (v) which is less than the decomposition potential of the electrolyte (≈ 1 V) is applied with positive polarity on the right side, the Ag^+ ions move initially from the right to the Ag electrode. Graphite acts as a blocking electrode so that there is no supply of Ag^+ ions at the C|Ag-rich interface. At the steady state, the potential gradient due to electric field is just balanced by the chemical potential gradient so that the ionic current is zero. Under these conditions the current is solely due to differential flow of electrons or holes. Wagner has shown that the
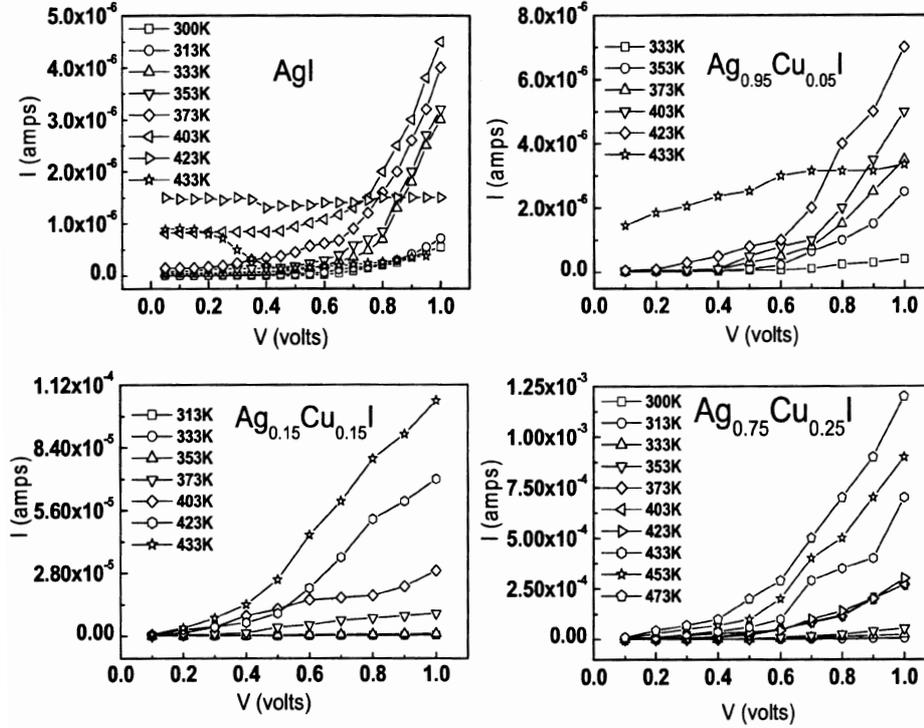
Figure 3. *I–V* characteristics of pure AgI and Ag-rich systems at various temperatures.

steady state current (I) is given by

$$I_{\mathrm{T}} = I_{\ominus} + I_{\oplus} = (RTA/LF)[\sigma_{\ominus}\{1 - \exp(-EF/RT)\} + \sigma_{\oplus}\{\exp(-EF/RT) - 1\}],$$ (1)

where I_{T} is the total electronic current passing through the cell under steady state condition, $I_{\ominus}$ and $I_{\oplus}$ are the current due to electrons and holes respectively, $\sigma_{\ominus}$ and $\sigma_{\oplus}$ are the conductivities due to electrons and holes respectively, E is the applied emf, F is the Faraday constant, R is the gas constant and, L and A are the specimen thickness and electrode area respectively.

Figure 3 shows the *I–V* characteristics of pure AgI and Ag-rich solid solutions at select temperatures in the range from 300 K to 493 K. Pure AgI solid solution shows a ramp-like current behavior up to 313 K and nonlinearity thereafter. The studies of Shahi and Wagner [10] which show nonlinear current–voltage characteristics of $(-)$Ag/α-AgI/C$(+)$ cells at 422 K is in accord with our present work. While, it is the residual current behavior below 0.57 V, the change in current behavior at the threshold voltage of 0.57 V implies that the voltage-induced hole current response is similar to that of a forward biased p-n junction. Threshold voltage decreased as the temperature was increased: from 0.57 V at 333 K to 0.48 V at 403 K. Below the phase transition temperature ($\leq$420 K), because $\sigma_{\ominus} \gg \sigma_{\oplus}$ the charge carriers
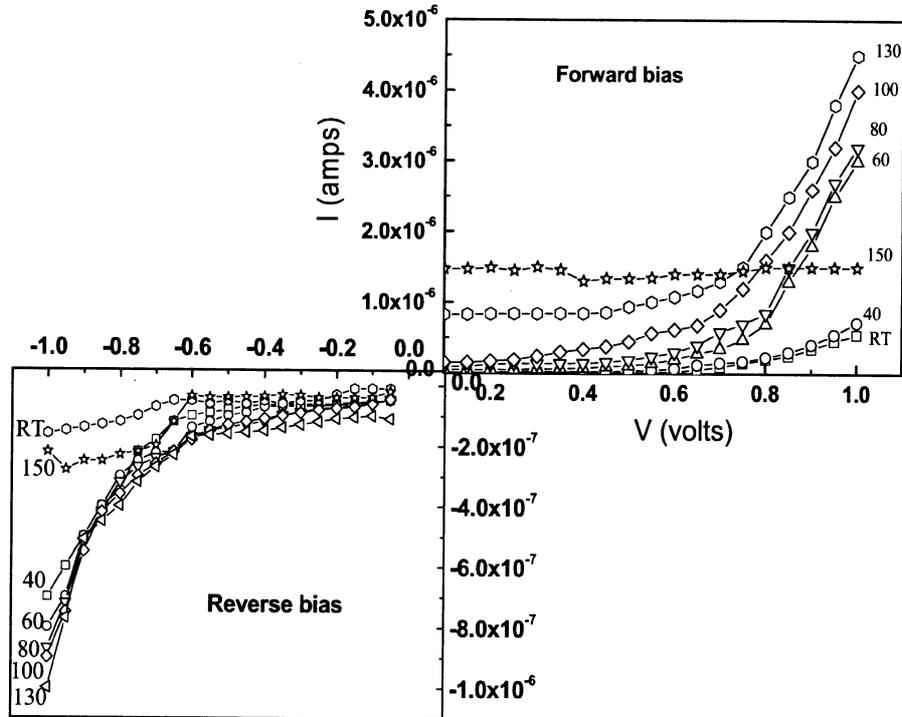
**Figure 4.** *I–V* characteristics show both the forward bias and the reverse bias of undoped AgI.

are predominantly electrons and hence the second term is negligible compared to the first in (1). Thus

$$I_{\mathrm{T}} = (RTA/LF)[\sigma_{\ominus}\{1 - \exp(-EF/RT)\}]. \qquad (2)$$

The current–voltage curves (figure 4) show diode-like behavior above 333 K to 403 K and the curves are nonlinear for both positive and negative voltages, which possibly arise from the interfacial microscopic p-n junctions which could be in the form of an array of metal–semiconductor nanojunctions generated by Ag metal particles and AgI semiconductors. Such a behavior is observed below the phase transition temperature while above the phase transition temperature it again shows a linear behavior because the charge carriers are now predominantly holes and the conduction is predominantly ionic. So, the first term in eq. (1) is negligible compared to second term. Thus,

$$I_{\mathrm{T}} = (RTA/LF)[\sigma_{\oplus}\{\exp(-EF/RT) - 1\}]. \qquad (3)$$

In our recent study on electron paramagnetic resonance (ESR) of pure AgI, a sharp resonance at $g = 2.0036$ was detected. Ag metallic particles which are formed during mechanochemical reaction process produce this resonance [5]. This has been further corroborated by our present study on electronic conductivity, because Ag
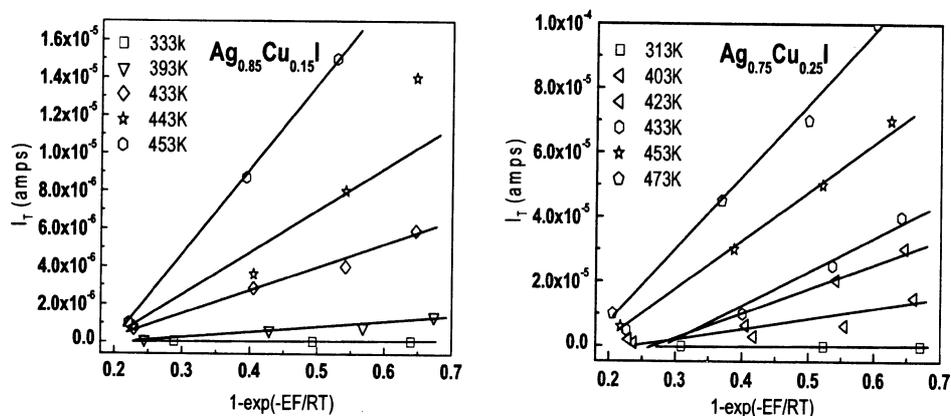
Figure 5. Total current (I_T) vs. $[1 - \exp(-EF/RT)]$ plots for Cu-doped AgI solid solutions corresponding to $Ag_{0.85}Cu_{0.15}I$ and $Ag_{0.75}Cu_{0.25}I$.

metal particles are responsible for nonlinear current–voltage behavior. Gravimetric measurements are useful when the solid compound has a large nonstoichiometry while the measurement of the electronic conductivity is effective when the conductivity of sample is quite sensitive to the chemical potential of its components. Mizusaki *et al* [11] obtained the electronic conductivity, the nonstoichiometry and apparent mobility of electronic carriers of AgBr and α-AgI using chemical diffusion coefficients.

The sudden rise in the current with the threshold voltage of 0.4 V in the order of 10^{-7}–10^{-6} A in a nonlinear manner in the $Ag_{0.95}Cu_{0.05}I$ solid solution, suggests that a substantial number of holes are injected by Cu atom to the Ag-rich solid solution. The number of holes injected by Cu atom increases as Cu concentration increases and this gives rise to the sudden change in the current–voltage behavior observed in the order of 10^{-4}–10^{-3} A. It is known that the Cu-rich compositions tend to contain holes and Ag-rich compositions contain electrons as current carriers in the I–VII mixed semiconductors (AgI is an n-type semiconductor, CuI is a p-type semiconductor).

In figure 5, the current (I_T) vs. $[1-\exp(-EF/RT)]$ plots exhibit straight lines at different temperatures for $Ag_{0.85}Cu_{0.15}I$ and $Ag_{0.75}Cu_{0.25}I$ solid solutions. Slopes deduced from these plots were equated to RTA/LF and thus the electronic conductivity ($\sigma_\ominus$) is calculated for all compositions. Log σ vs. $1000/T$ plot for all compositions shown in figure 6, reveals that the electronic conductivity increases with increasing temperature upto 423 K and above that temperature electronic conductivity drops in order to transform from electronic to ionic current. The reason for this could be because the ionicity of α phase is larger than the γ phase above 423 K. The broken line shows the structural phase transition. Unfortunately we could not go beyond 433 K due to electrode–electrolyte contamination. The dominant effect of increase of temperature is to increase the electron mobility in AgI influenced by the formation of lattice defects created by mechanochemical reaction process. In addition, electronic conductivity also increased as the percentage of Cu concentration increased with temperature because the number of electronic current
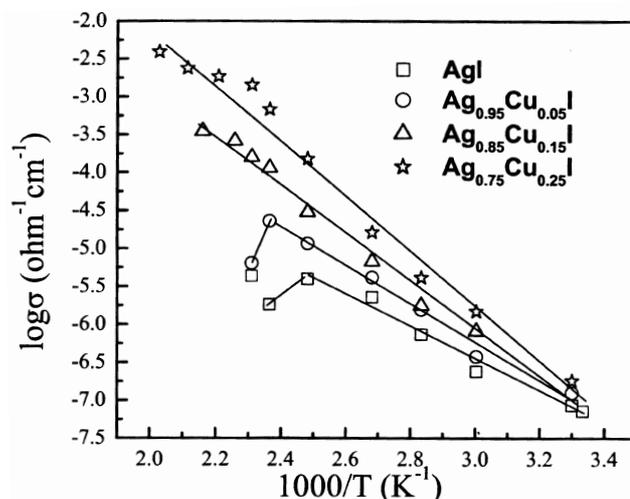
Figure 6. A plot of log σ vs. $1000/T$ for undoped AgI and Cu-doped AgI solid solutions showing a linear curve.

carriers/holes are predominantly injected by Cu while replacing Ag^+ cation from the lattice sites in AgI. γ-AgI has a Frenkel defect formation energy comprising of an interstitial formation energy and a vacancy formation energy. According to the defect model of AgI proposed by Lieser [12], for γ-AgI the Ag^+ ion leaving from the normal sites in thermal equilibrium is situated at tetrahedral position of interstitial sites. Since CuI has no Frenkel defects below 473 K it substantially reduces the concentration of the Frenkel defects in AgI at low temperature and finally the electronic charges are carried by Cu^+ ion acting as an impurity mobile ion.

From figure 6, electron activation energies obtained from slope were $E_a = 0.48$, 0.6, 0.74 and 1.01 eV for AgI, $Ag_{0.95}Cu_{0.05}I$, $Ag_{0.85}Cu_{0.15}I$ and $Ag_{0.75}Cu_{0.25}I$ solid solutions respectively. A plot of activation energy (E_a) vs. Cu concentration is shown in figure 7. Undoped AgI shows very low activation energy of 0.48 eV and an increase in activation energy of 1.01 eV is observed after 25% Cu doping. It is interesting to compare these values with those obtained by Mazumdar *et al* [13] who found $E_a = 0.46$ eV for undoped HI-grown AgI. Webb *et al* [14] obtained at low temperature >200 K, a DC activation energy of 0.29 eV for pure β-AgI and in this region the conductivity is independent of applied frequency. Since Cu has a very small atomic radius (128 pm) when compared to Ag (144 pm), it has been found that Cu in AgI contracts the lattice of AgI and consequently lattice defect formation takes place during mechanochemical reaction process. This would probably increase the activation energy for the electronic conductivity in a contracted lattice.

4. Conclusions

Using DC polarization technique the electronic conductivity measurement has been carried out for undoped AgI and $Ag_{1-x}Cu_xI$ (where $x = 0.05, 0.15, 0.25$) solid
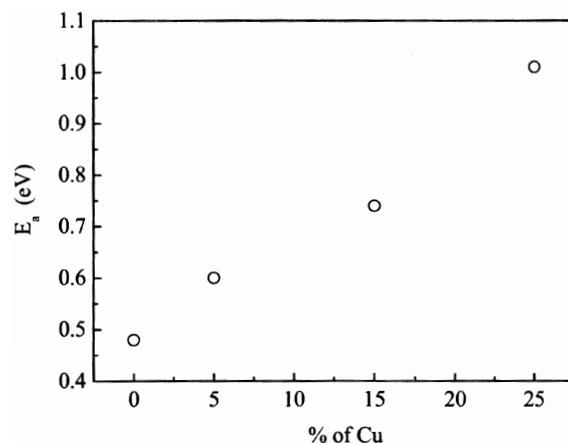
Figure 7. A plot of activation energy (E_a) vs. percentage of Cu-concentration showing an increase in activation energy with Cu concentration.

solutions in the temperature range 300–473 K. A diode-like current–voltage characteristics arises from microscopic p-n junctions and an enhanced electronic conductivity of the order of 10^{-3}A is observed for undoped AgI and Cu-doped AgI respectively. Activation energies for electron transport obtained from log σ ($\Omega^{-1}cm^{-1}$) vs. $1000/T$ (K^{-1}) were E_a = 0.48, 0.6, 0.74 and 1.01 eV for AgI, $Ag_{0.95}Cu_{0.05}I$, $Ag_{0.85}Cu_{0.15}I$ and $Ag_{0.75}Cu_{0.25}I$ solid solutions respectively. The near-twofold increase in activation energy (1.01 eV) observed upon 25% Cu doping is due to the substantial concentration of current carriers/holes injected by Cu while replacing Ag^+ in AgI. These materials probably act as nanodiodes while those between a nanometal and a nanosemiconductor could yield a Schottky barrier.

Acknowledgments

References

[1] G Dittmer, *Thin Solid Films* **9**, 317 (1972)
[2] H Birey, *Appl. Phys. Lett.* **23**, 316 (1973)
[3] A Dan, B Satpati, P V Satyam and D Chakravorthy, *J. Appl. Phys.* **93**, 4794 (2003)
[4] D Bharathi Mohan and C S Sunandana, *J. Phys. Chem. Solids* **64**, 1669 (2004)
[5] D Bharathi Mohan and C S Sunandana, *J. Phys. Chem.* **B110**, 4659 (2006)
[6] S Chandra, *Superionic solids: Principles and applications* (North Holland, Amsterdam, 1981)
[7] K V Kiukkola and C Wagner, *J. Electrochem. Soc.* **104**, 379 (1957)

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 [8] M M Hebb, *Chem. Phys.* **20**, 185 (1952)
 [9] C Wagner, *J. Electrochem. Soc.* **60**, 4 (1956)
[10] K Shahi and J B Wagner, *J. Electrochem. Soc.* **128**, 6 (1981)
[11] J Mizusaki, K Fueki and T Mukaibo, *Bull. Chem. Soc. Jpn.* **52**, 1890 (1979)
[12] K H Lieser, *Fortscher. Mineral* **36**, 96 (1958)
[13] D Mazumdar, P A Govindacharyulu and D N Bose, *J. Phys. Chem. Solids* **43**, 933 (1982)
[14] J B Webb, M Sayer and A Mansingh, *Solid State Commun.* **25**, 431 (1978)