DC Conductivity of Fe_2O_3-TeO_2 Amorphous Films Prepared by Vapor Deposition Method

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Date of Submission: 28th Feb, 2014 Date of Acceptance: 3rd March, 2014

Abstract

Fe_2O_3-TeO_2 films were prepared using vapor deposition technique and dc conductivity was studied in the temperature range 323-513K for different compositions. X-ray diffraction study confirms the amorphous nature of the films. It was observed that the conductivity of the films at 323K varies from 3×10^{-2} to 5×10^{-3}Scm^{-1}. The Seebeck co-efficient study indicates that the films are n-type semiconductor. Mott's small polaron non-adiabatic hopping conduction mechanism was valid above 380K and variable range hopping at lower temperature. XPS analysis confirm the presence of Fe^{2+} and Fe^{3+} and hopping of electrons occurs between these two ionic states.

Keywords: dc conductivity, XRD, XPS

1. Introduction

TeO_2 based glasses are important for many possible electrical and optical applications[1,2]. Addition of transition metal ions in TeO_2 based films are very promising for memory switching devices and cathode materials for batteries[3,4]. TeO_2 is a conditional glass former and its attractive properties arise from the special structural characteristics. It has been demonstrated that amorphous TeO_2 and crystalline TeO_2 consists of three dimensional network of TeO_4 structural units. The TeO_4 unit is a trigonal in which one of the Te sp^3d hybrid orbital is occupied by an electron lone pair while the other two equatorial position and two axial positions are occupied by four oxygen atoms. Introduction of modifier breaks TeO_4 network into Te-O-Te bonds together with new structural units such as TeO_3 with non-bridging oxygen. The TeO_3 unit is a trigonal pyramid, in which an electron lone pair occupies one of the Te sp^3 higher orbital. Glasses containing Fe_2O_3 are semiconducting in nature and transport and magnetic properties have been investigated extensively[5,6]. Conductivity of these glasses arises due to small polaron hopping conduction which are several orders of magnitude higher than silicate, borate glasses containing same amount of Fe_2O_3. Conductivity of Fe_2O_3-TeO_2 glasses are higher than that of MoO_3-TeO_2 glasses[7]. Due to high stability and different valence state of Fe, conduction mechanism of Fe_2O_3-TeO_2 films is very important. It is expected that the conductivity of Fe_2O_3-TeO_2 films is higher than that of MoO_3-TeO_2 films.

2. Experimental Procedure

Fe_2O_3-TeO_2 amorphous films have been prepared by resistance heating evaporation technique using a commercial vacuum coating unit. Glass were prepared using reagent grade Fe_2O_3 and TeO_2 with 99.9% purity for different molar ratio as 5:95, 10:90, 15:85, 20:80 in an electrical furnace at 1073-1173K for 30 min. in air. The melt quenched glass was made powder by grinding in an agate mortar and used for evaporation in a vacuum unit at a pressure 5×10^{-6} torr by passing current 180A for 15min. The films are coated on ultrasonically cleaned non-alkali glass substrate (AN-glass, product of Asahi glass Co. Ltd, 0.7mm thickness) maintained at temperature 373K. The target and substrate distance was maintained at 25cm.

The characterization of the films was studied by x-ray diffraction (Philips, X'pert system PW 1830). Thickness of the films was measured using a contact needle type surface roughness measuring tester (Deltac-3, ULVAC, Chigasaki, Kanagawa, Japan) and found in the range 250-360 nm. X-ray photoelectron spectroscopy (XPS) study performed using ULVAC-PHI XPS spectrometer, (Chigasaki, Kanagawa, Japan) after 10s sputtering in Ar atmosphere.

The dc electrical conductivity was performed by measuring temperature and current with a digital thermometer (Advantest, TR 2114) and a Keithley electrometer (Model 614) respectively after application of a fixed voltage. The Seebeck co-efficient of the films was determined by measuring the thermoelectric power between two copper constantan thermocouples attached to the samples with temperature difference 5-10K.

3. Results and Discussion

Fig.1 shows the X-ray diffraction pattern for different compositions of the films using

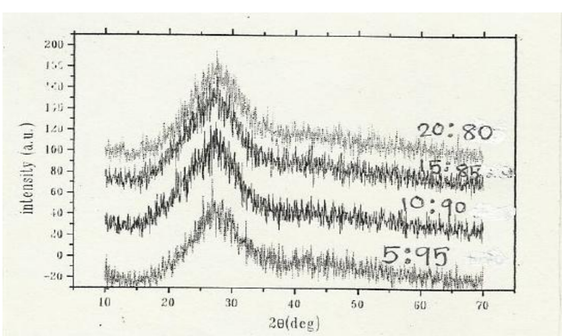

Fig. 1 XRD pattern of the as deposited

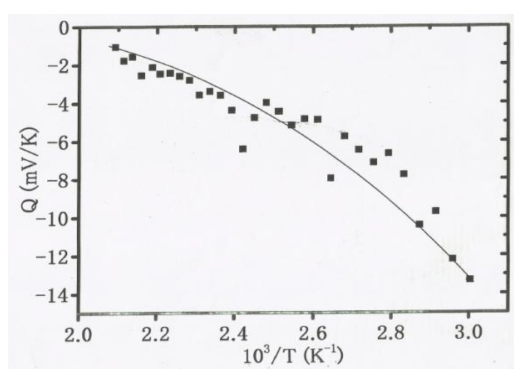

Fig.2 TEP of $20Fe_2O_3$-$80TeO_2$ films

CuK_{α} radiation exhibiting a broad hump at 25-27^{o} indicating an amorphous structure.

Fig.2 shows the thermoelectric power for 20:80 films. It is confirmed that the films are n-type semiconductor due to negative Seebeck co-efficient.

Fig.3 shows the XPS spectra of amorphous $20Fe_2O_3$-$15TeO_2$ film. Fe peaks are ascribed as Fe, Fe^{2+}; Fe_3O_4 and Fe^{3+} at binding energy 706.67, 709.17, 710.38 and 712.15eV respectively. The area of the peaks Fe_3O_4 and Fe described as 13.11% and 11.79%. Neglecting these two peaks in respect to other peaks Fe^{2+} and Fe^{3+} the calculated reduced Fe ion ratio for 20:80 $C_{Fe} = \frac{Fe^{2+}}{Fe^{2+} + Fe^{3+}}$ = 0.42. From these it is confirmed that charge transport occurs due to different valence state Fe^{2+} and Fe^{3+}.

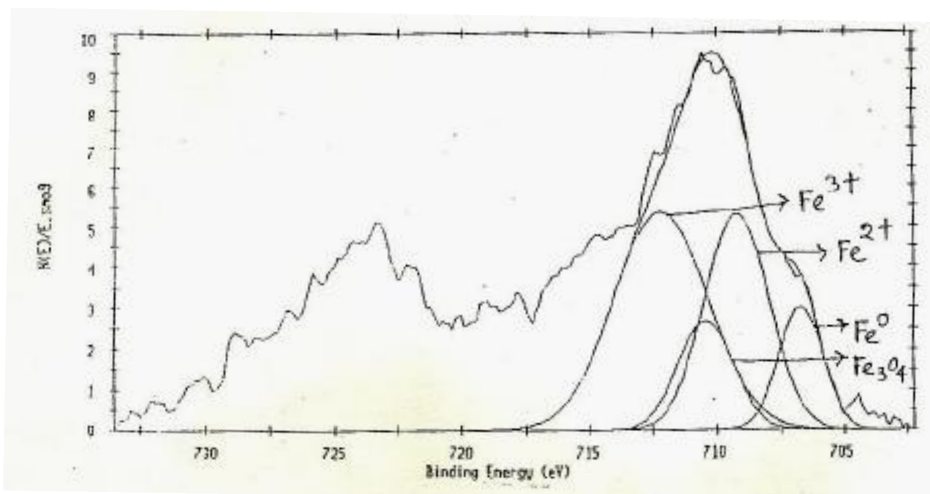

Fig.3 XPS spectra of $20Fe_2O_3$-$80TeO_2$ films

At 323K the conductivity of the films varies from 2×10^{-2} to $5\times10^{-3}Scm^{-1}$. The conductivity of the films increases with increase of temperate for all films and follows Mott's small polaron hopping conduction model[8]. The temperature dependence of electrical conductivity σ_{dc} for different film compositions is described in the temperature range (380-513K) as $\sigma = (\sigma_o/T) \exp(-W/kT)$; where σ_o is the pre-exponential factor and W is the activation energy for conduction. The experimental temperature (256K) and estimated temperature (453K) obtained from logσ vs. W (Fig.4) can be concluded that the present films are due to non-adiabatic small polaron hopping. The conductivity of the films increases with increase of Fe_2O_3 content. Variable range hopping (VRH) proposed by Mott is valid in the temperature above 300K is based on single optical phonon approach. In this model σ is given by

$\sigma = B \exp(-A/T^{1/4})$; where $A = 4[2\sigma^3/9\ \pi k N(E_F)]^{1/4}$ and $B= [e^2/2(8\pi)^{1/2}]\nu_o[N(E_F)/\alpha kT]^{1/2}$

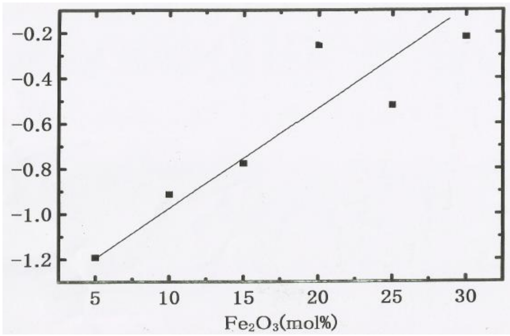

Fig.4 **log σ vs. Fe_2O3 (mol%) of the of Fe_2O_3- TeO_2 films at 253K**

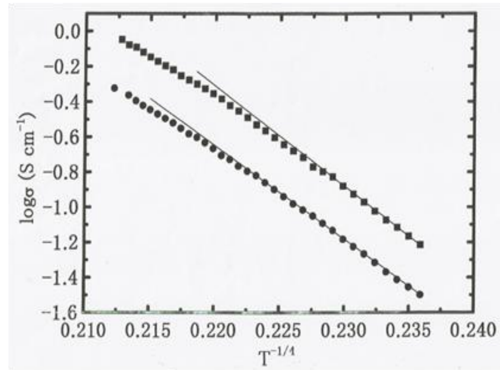

Fig.5 Plot of log σ against $T^{-1/4}$ of Fe_2O_3-TeO_2 films for 15:85(•) and 20:80(□)

$N(E_F)$ is the density of states at the Fermi level of the order of $10^{21}eV^{-1}cm^{-3}$ except for 10:90 films is of 10^{24}. Some electrical parameters are given in Table-2

Table-2: Mott's parameters for Fe_2O_3-TeO_2 films from conductivity data

Fe_2O_3:TeO_2	Thickness (nm)	σ_{dc}(300K) (Scm^{-1})	W(eV)	$N(E_F)$($eV^{-1}cm^{-3}$)	R_{VRH} (Å)	W_o(eV)
5:95	501	5.08×10^{-3}	0.283	4.75×10^{21}	5.945	0.239
10:90	261	4.84×10^{-2}	0.203	5.19×10^{24}	1.034	0.042
15:85	301	3.05×10^{-2}	0.253	7.93×10^{22}	2.941	0.118
20:80	352	5.49×10^{-2}	0.235	5.72×0^{21}	5.676	0.228
25:75	363	3.17×10^{-2}	0.258	6.71×10^{21}	5.342	0.215

For VRH conduction R_{VRH} >>1 and W_o>>kT. For the present films R= 1.0-6.0 and W_0= 0.12 - 0.24eV. These parameters confirm VRH conduction in the present films at high temperature.

4. Conclusion

We have successfully prepared Fe_2O_3-TeO_2 films using vapor deposition technique. X-ray diffraction study confirms the amorphous nature of the films. Electrical conductivity and Seebek study indicates that the films are n type semiconductor. Mott's small polaron non-adiabatic hopping conduction mechanism was valid above 380K and variable range hopping above room temperature. XPS analysis confirms the presence of Fe^{2+} and Fe^{3+} and hopping of electrons occurs between these two ionic states.

References

1. T. Nishida, M.yamada, T.Ichii and Y. Yakashima, *Jpn.J. Appl. Phys*. **30,** 768 (1991).
2. I. Shaltout, YI-Tang, R. Braunstein and E.E. Shaisa, J. Phys. Chem. Solids, **57,** 1223 (1996).
3. Manisha Pal, K. Hirota and H. Sakata*; Phys. Stat Sol (a)* **196**, 396 (2003).
4. A. Ghosh, *J. Appl. Phys*., **64**, 2652(1998).
5. A. Mekki, G.D.khattak, L.E.Wenger, *J. Non-Crys.Solids*, **352**, 3326 (2006).
6. H.Satao, H. Sakata, *Mat. Chem & Phys*. **65,** 186(2000).
7. Manisha Pal, K. Hirota, Y. Tsujigami and H. Sakata; *J. Phys. D, appl. Phys*. **34,** 459 (2001).
8. I.G.Austin and N.F.Mott, *Adv.Phys*. **18**, 41 (1969).