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Some properties of thin layers of silica containing carbon and iron oxides prepared by the sol–gel method

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Thin layers of silica containing carbon and iron oxides have been prepared by the sol–gel method. The samples were investigated using Auger electron spectroscopy, energy loss, microhardness and Mössbauer effect measurements. It is shown that carbon is located in the pores of the silica network. The electrical conductivity depends on the temperature of heat treatment in the vacuum. The maximum value of conductivity was observed for an annealing temperature about 600 to 800° C. All samples exhibited low activation energy ~ 0.12 eV. It is suggested that the mechanism of conductivity can be interpreted as a tunnelling process of electrons between carbon granules.

1. Introduction

Glassy coatings of oxide can be prepared at a relatively low temperature using a sol–gel method by a dip-coating process. To date, a wide range of coloured silica coatings containing different transition metal oxides have been prepared. The main aim of these works was to study the optical properties of these films. Several reviews have been published which were devoted to the optical properties of the coloured coatings, but on the other hand, little information exists on the electrical properties of silica films containing transition metal oxides [1–3].

It is well known that glasses containing large amounts of transition metal ions exhibit semiconducting properties [4]. This behaviour can be observed if transition metal ions exist in a different valency state in a glassy matrix. The mechanism of electron transport is electron hopping between ions in a different valency state, namely $V^{4+} \rightarrow V^{5+}$ or $Fe^{2+} \rightarrow Fe^{3+}$.

Silica layers can contain a relatively large amount of transition metal oxides. For example, oxide films containing more than 20 mol % VO_2, Fe_2O_3, CoO, CuO, Mn_2O_3, NiO have been prepared by a sol–gel method [3, 5, 6]. However, because of the low temperature of preparation, only one valency state (V^{4+}, Fe^{3+}, . . .) of the transition ion is observed. In this case the conductivity of the sample is very low. In order to increase the conductivity, various heat treatments have been applied in the preparation procedure.

Silica films containing iron oxide heated in vacuum exhibit very interesting electrical properties. We have found that this heat treatment leads to the formation of silica layers containing a large amount of carbon. In this paper we present the electrical properties of these films and the results of some additional experiments such as Mössbauer, microhardness, Auger spectroscopy, and energy loss measurements, which can explain the nature and the role of carbon in these layers.

2. Experimental procedure

The solution was prepared in two steps. First, iron-acetylacetonate, Fe $(acac)_3$ was dissolved in ethanol. Then a solution containing tetraethylorthosilicate (TEOS) with water and catalysts (HCl with acetic acid) was prepared. The two solutions were mixed together for 2 h at 60° C.

To obtain 80 mol % SiO_2 + 20 mol % FeO glass composition, the following molar ratio of TEOS: H_2O: EtOH: $Fe(acac)_3$: HCl; AcOH was used: 1 : 4 : 40 : 0.25 : 008 : 0.02. A dip-coating method was used to obtain thin films (0.1 to 0.2 μm) on a silica glass substrate. After drying at 80° C in air the samples were carbonized in vacuum (10^{-4} mm Hg) for about 0.5 h at different temperatures: 400, 600, 800, 900 and 1000° C. These heat treatments lead to the formation of a black and hard glassy layer containing 80 mol % SiO_2 + 20 mol % FeO. The microhardness of the layer was determined using the Vickers method. For d.c. conductivity measurements, parallel silver electrodes were evaporated at a distance of 1 mm. The electrical conductivity measurements were carried out in a special chamber under vacuum (10^{-2} mm Hg). Conversion electron Mössbauer spectroscopy has

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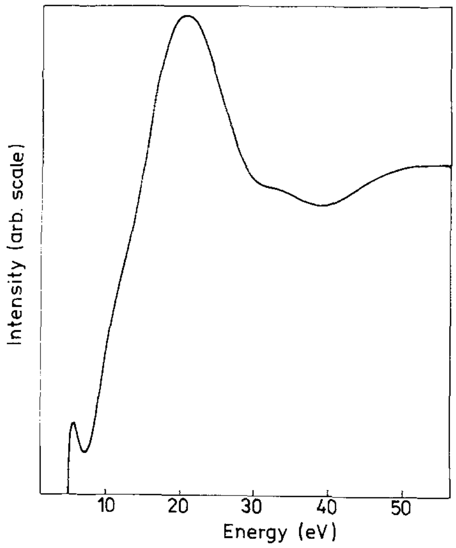

Figure 1 Electron energy loss spectrum of carbon for the sample heated at 900° C in vacuum.

been applied to identify the oxidation state and location of iron in the layer. In this method, electrons instead of γ-rays are resonant sensors. After resonant Mössbauer absorption of 14.4 keV γ-rays, ^{57}Fe nuclei are de-excited with the emission of 7.3 keV conversion electron or 5.6 keV Auger electrons. The penetration of such low-energy electrons in solids is about 0.2 to 0.3 μm, therefore it is possible to study thin films or surface properties of bulk samples. More details of this method are given by Sawicki and colleagues [7, 8].

The information on the nature of carbon was obtained by Auger electron spectroscopy (AES) and electron energy loss measurements.

3. Results

3.1. Auger electron spectroscopy and energy loss measurements

In order to obtain qualitative information about the surface of the sample, AES spectra were studied. We observed that carbon atoms are the predominant agents in our films. The carbon peak is similar to AES of graphite [9].

It is difficult to deduce full information on the structure of carbon from the AES. However, this can be obtained from the electron energy loss measurements. Robertson [10] has shown that energy loss for graphite as well as for various amorphous carbons and diamond are different. The loss function can show features due to one-electron inter-band transition and due to plasma oscillations of the valence electrons. It can be shown that the loss spectrum generally consists of two peaks, a lower peak assigned to π oscillations and an upper peak due to oscillations of all valence electrons ($\pi + \sigma$). The position of the lower peak around 6 eV is well established in graphite and amorphous carbon films, while in diamond only one peak at about 30 to 32 eV has been observed. Usually, this peak is shifted to the low-energy range and is located between 20 and 27 eV depending on the form of carbon. In our case (Fig. 1), this peak occurs at 21 eV which is a typical position for glassy carbon [11]. However, the lower peak is more pronounced in our spectrum and it may indicate that some graphite or other form of carbon can exist in our films. The supposition that the layer contains some non-graphitizable forms of carbon may be confirmed by microhardness measurements. Our preliminary results showed that an increase in hardness was obtained with an increase of the annealing temperature. For the sample heated at 1000° C in vacuum the Vickers hardness number (VHN) was about 910 while for the silica glass substrate, VHN was about 710. These measurements were performed using a load of 100 g.

3.2. Conversion electron Mössbauer spectroscopy

The iron (III) state and iron (II) state in glasses can easily be identified on the basis of different isomer shifts (IS) and quadrupole splittings (QS) in Mössbauer spectra [12, 13]. Fig. 2 shows the conversion electron Mössbauer spectra of ^{57}Fe in the sample heated at 900° C in vacuum. The analysis of this spectrum shows that iron ions exist in the layer in the Fe^{2+} state only. The Fe^{2+} isomer shift (1.11 mm sec^{-1}) and quadrupole splitting (2.05 mm sec^{-1}) are typical for Fe^{2+} ions in silica and phosphate glasses [13]. The sample heated at 400° C in air (Fig. 3) contains Fe^{3+} ions only. The values of IS = 0.36 mm sec^{-1} and QS = 1.05 mm sec^{-1} are also typical for ferric ions in glasses. In both cases the values of IS indicate that Fe^{2+} as well as Fe^{3+} exist in octahedral coordination in our films [13, 14].

Therefore, one can conclude that iron ions are glass modifiers. Similar results of Mössbauer effect investigations for SiO_2–Fe_2O_3 glasses made by a sol–gel method have been published by Yoshio *et al.* [15] and by Guglielmi *et al.* [16].

3.3. d.c. conductivity

Fig. 4 shows the results of surface d.c. conductivity measurements for the samples heated in vacuum at

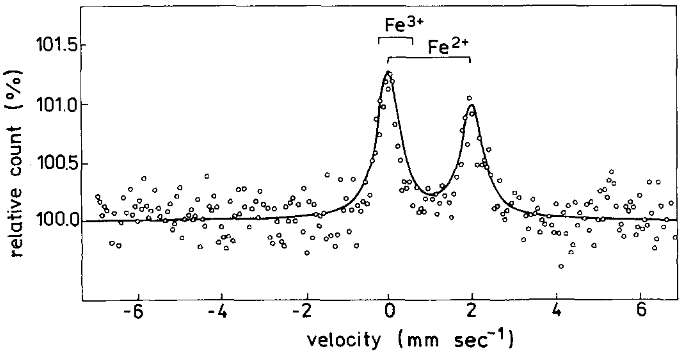

Figure 2 Conversion electron Mössbauer spectrum of ^{57}Fe in the sample heated at 900° C in vacuum.

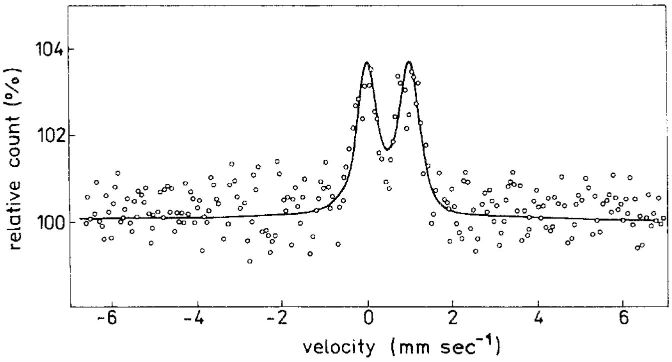

Figure 3 Conversion electron Mössbauer spectrum of ^{57}Fe in the sample heated at 400° C in air.

temperatures: 400, 600, 800, 900 and 1000° C. Change of heat-treatment temperature from 400 to 600° C increases the conductivity by about five orders of magnitude (Fig. 5). For samples heated at 800 and 900° C a maximum conductivity was observed.

Annealing at 1000° C leads to a drastic change in conductivity which decreases by about nine orders of magnitude. For all the films studied, the activation energy is low 0.08 to 0.12 eV.

4. Discussion

The experimental results of AES, as well as Mössbauer effect, showed that conductivity in our films was strictly connected with carbonization of the organic residue of the starting solutions. The formation of a thin silica layer by a sol–gel method takes place through hydrolysis–polycondensation processes. During these reactions the more volatile compounds, such as alcohol and water, evaporate leading to the formation of a porous silica network. It has been confirmed from Mössbauer spectra that iron ions are the glass modifiers. This may suggest that organic groups of Fe(acac)$_3$ are located and carbonized within the pores. The sintering in vacuum converts the gel into glass. During this process very high capillary forces may favour the formation of some form of the non-graphitizated carbon.

Energy loss and microhardness measurements indicate that the glassy carbon can exist in our films. Glassy carbon exhibits a metallic conduction of the order of 10^2 to $10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$ [10]. Therefore, one can assume that our films are nonhomogeneous with randomly distributed granules of glassy carbon in a silica network. This structure may be similar to discontinuous metal structures usually prepared by the evaporation or sputtering of a metal on to a glass surface [17–19], or granular structures on the surface in lead silicate glasses after reduction in a hydrogen atmosphere [20].

The commonly accepted theoretical model of the electrical conductivity in discontinuous metal structures is based on the tunnelling process of electrons between metal granules [17, 18]. It is believed that creation of the charge carriers is due to thermal processes leading to the transfer of electrons from one metal granule to a neighbouring one.

The energy, E_c, for the creation of two granules, one positively charged, the second negatively charged, is described by the equation

$$E_c = \frac{e^2}{4\pi\varepsilon\varepsilon_0 d} F(s, d)$$

where d is the diameter of the granules, s the distance between two granules, ε the dielectric constant of glass

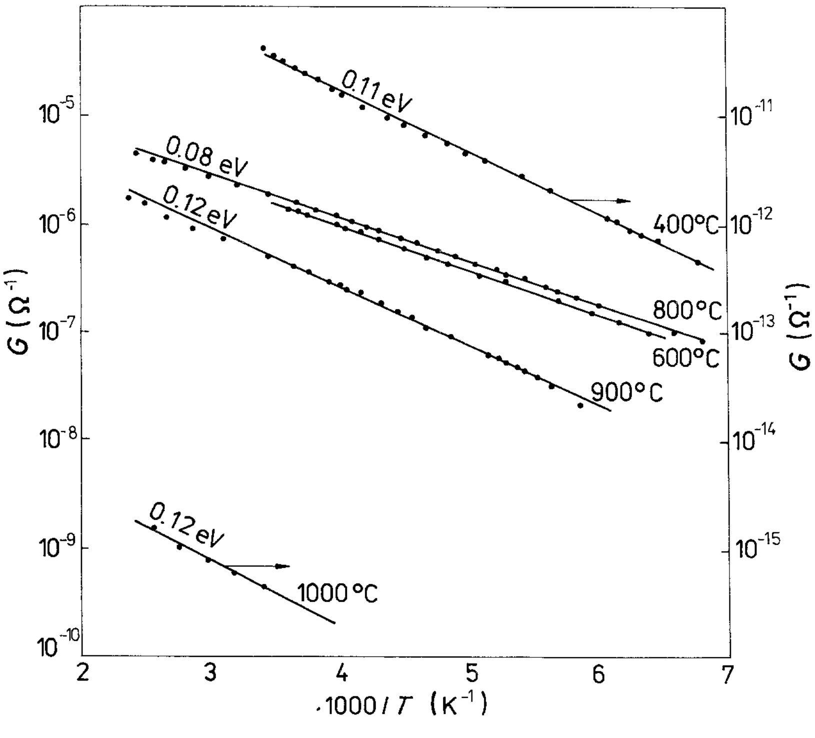

Figure 4 d.c. conductance as a function of inverse temperature for the samples of different annealing temperatures in vacuum.

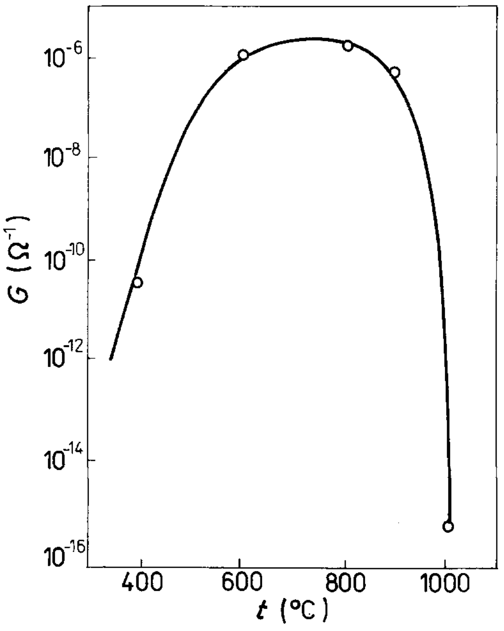

Figure 5 Room-temperature d.c. conductance as function of annealing temperature in vacuum.

matrix, and $F(s, d)$ a function which depends on the distribution of size and distances between granules. Hill and Coutts [21] showed that for a variety of size $f(d)$ and distance $f(s)$ distributions, conductivity–temperature dependences may be obtained in the form $\ln \sigma \simeq T^{-n}$ where $1/3 \leqslant n \leqslant 1$.

Our results of d.c. conductivity measurements obeyed the $\ln \sigma \simeq T^{-1}$ law with an activation energy of 0.08 to 0.12 eV. This suggests that the electrical conductivity in silica film containing carbon can be interpreted as a tunnelling process between glassy carbon granules.

References

1. H. SCHROEDER, *Phys. Thin Films* **5** (1969) 87.
2. H. DISLICH, *J. Non-Cryst. Solids* **57** (1983) 371.
3. S. SAKKA, *Trans. Indian Ceram. Soc.* **46** (1987) 1.
4. L. MURAWSKI, C. H. CHUNG and J. D. MACKENZIE, *J. Non-Cryst. Solids* **32** (1979) 91.
5. A. DURAN, J. M. FERNANDEZ NAVARRO, P. CASARIEGO and A. JOGLAR, *ibid.* **82** (1986) 391.
6. F. ORGAZ and H. RAWSON, *ibid.* **82** (1986) 378.
7. J. SAWICKI, B. SAWICKA and O. GZOWSKI, *Phys. Status Solidi* (*a*) **41** (1977) 173.
8. J. A. SAWICKI, *Mater. Sci. Engng.* **69** (1985) 501.
9. G. E. McGUIRE and P. H. HOLLOWAY, in 'Electron Spectroscopy: Theory, Techniques and Applications', edited by C. R. Brundle and A. D. Baker (Academic, London, 1981) p. 52.
10. J. ROBERTSON, *Adv. Phys.* **35** (1986) 317.
11. F. R. McFEELY, S. P. KOWALCZYK, L. LEY, R. G. CAVELL, R. A. POLLAK and D. A. SHIRLEY, *Phys. Rev. B* **9** (1974) 5268.
12. C. R. KURKJIAN, *J. Non-Cryst. Solids* **3** (1970) 157.
13. J. M. D. COEY, *J. Physique* (*Suppl. 12*) **35** (1974) C6-89.
14. L. MURAWSKI, *J. Mater. Sci.* **17** (1982) 2155.
15. T. YOSHIO, C. KAWAGUCHI, F. KANAMARU and K. TAKAHASHI, *J. Non-Cryst. Solids* **43** (1981) 129.
16. M. GUGLIELMI, A. MADDALENA and G. PRINCIPI, *J. Mater. Sci. Lett.* **2** (1983) 467.
17. C. A. NEUGEBAUER and M. W. WEBB, *J. Appl. Phys.* **33** (1962) 74.
18. B. ABELES, PING SHENG, M. D. COUTTS and Y. ARIE, *Adv. Phys.* **24** (1975) 407.
19. J. E. MORRIS and T. J. COUTTS, *Thin Solid Films* **47** (1977) 3.
20. O. GZOWSKI, L, MURAWSKI, K. TRZEBIATOWSKI, *J. Phys. D.* **15** (1982) 1097.
21. R. M. HILL and T. J. COUTTS, *Thin Solid Films* **42** (1977) 201.

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