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Electron spin resonance studies of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films

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Electron spin resonance studies of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 amorphous thin films have been made. For lower molar contents of B_2O_3, the co-evaporated V_2O_5/B_2O_3 films show poorly resolved hyperfine structure, whereas for higher content of B_2O_3 the hyperfine spectra are well resolved. This behaviour of films is attributed to the increase in the lifetime of a particular V^{4+} ion due to Anderson localization of charge, as the degree of disorder increases with increase in the molar content of B_2O_3. The unpaired electron at a given time is localized on a single ^{51}V nucleus. The low intensity of ESR signal for higher concentration of V_2O_5 in the co-evaporated V_2O_5/B_2O_3 films has been related to the less effective concentration of V^{4+} ions due to antiferromagnetic coupling of the V^{4+} ions.

1. Introduction

Electron spin resonance (ESR) studies can be employed as a useful source of information about the structure and electronic states of transition metal oxide glasses. Generally a single asymmetric broad line without fine structure is observed in the ESR spectra of transition metal oxides. Some authors [1–3] related the asymmetric character of an ESR signal to a non-symmetric g tensor. ESR studies with a symmetric signal can be used to estimate the concentration of such states, but asymmetric or hyperfine structure can provide information on the nature of the paramagnetic centres. The ESR technique has been found to be very helpful in understanding the interactions between unlike magnetic ions in amorphous solids, as well as for finding correlation between the formation of associates of dissimilar transition metal ions and the electrical properties of semiconducting glasses containing transition metal oxide [4].

Some defects are normally observed in the lattice of vanadium pentoxide leading to the formation of lower oxide states which can be detected by the ESR technique [5]. The electrical conduction in V_2O_5 occurs due to hopping of unpaired electrons between V^{4+} and V^{5+} ions [6–8]. Tilly and Hyde [9] and Colpaert *et al.* [10] reported the formation of lower oxides, such as the structures V_2O_9 and V_6O_{13} on the reduction of V_2O_5. Michaud *et al.* [11] proposed that the short range order around V^{4+} ions is the same in both hydrated V_2O_5 and orthorhombic V_2O_5. They proposed that the disorder in the amorphous phase leads to a localization of charge carriers, the electron mobility being about ten times smaller than in crystalline V_2O_5. The hydrated V_2O_5 showed a hyperfine structure due to the interaction of 3d ($s = 1/2$) electrons and the nuclear spins ($I = 7/2$) of the vanadium nuclei. Some authors [12, 13] observed a hyperfine structure consisting of 15 equally spaced lines in the ESR spectra of simple V_2O_5, indicating that the unpaired electron is trapped on two vanadium sites associated with oxygen vacancies arising from non-stoichiometry of the oxide and the wavefunction of this electron is delocalized over these two vanadium sites. Kahn *et al.* [14], from ESR studies, proposed that in crystalline V_2O_5, the unpaired 3d electron is delocalized on four vanadium nuclei, whereas for amorphous V_2O_5 it is localized on only one vanadium nucleus. Szorenyi *et al.* [15] reported that amorphous V_2O_5 films prepared by the chemical vapour deposition method, showed a partially resolved hyperfine pattern of ESR spectra of V^{4+} when measured at room temperature, whereas the spectra were well resolved when measured at low temperature.

Henri *et al.* [16] observed eight hyperfine lines in the ESR spectrum of amorphous V_2O_5 doped with 0.5 mol % WO_3, and the spectrum remained invariant with the temperature in the range 4–300 K as a result of the Anderson localization of charge carriers. On the other hand, the width of the lines of the hyperfine spectrum of crystalline V_2O_5 doped with the same percentage of WO_3 was strongly temperature-dependent. It increased with the temperature and all lines collapsed above 200 K which was attributed to the lifetime broadening effect due to the hopping of electrons between V^{4+} and V^{5+} ions. They reported that in both the cases the unpaired electron was localized on a single vanadium site, giving rise to a V^{4+} ion. Similarly, Henri *et al.* [17] investigated the ESR spectra of a single crystal of V_2O_5 doped with 0.05 mol % of WO_3 and suggested the presence of two paramagnetic centres. One gave rise to eight hyperfine lines due to an unpaired electron trapped on a single V^{4+} site adjacent to a W^{6+} site. Another broad signal appeared above 90 K and was related to another paramagnetic defect where an unpaired electron is delocalized around the W^{6+} ion. Pasturel *et al.* [18] reported a well-resolved 15-line hyperfine line spectrum for pure V_2O_5, but after a lithiation process of

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V_2O_5, the hyperfine spectrum progressively disappeared and after a few hours converted into a single ESR line. On the other hand, the ESR spectrum was drastically modified when the crystal was heated in air and showed a 29-hyperfine-line ESR signal. Ioffe and Patrina [19, 20] noticed that an unpaired electron in V_2O_5 may interact with one, two or four ^{51}V nuclei, depending upon the nature of the impurities and on the way in which they are incorporated into the lattice. They further suggested that the disappearance of hyperfine lines on increasing the temperature from 77 K to room temperature could be attributed to the predomination of electron–phonon interaction at room temperature. Hosseini and Hogarth [21] recorded single lines in the ESR spectra of V_2O_5–P_2O_5 and V_2O_5–P_2O_5–TeO_2 glasses. Sanchez *et al.* [22] studied the ESR spectra of V_2O_5 doped with lithium and observed 29 hyperfine lines in the ESR spectra. He suggested that the unpaired electron is trapped on four vanadium sites around the Li^+ impurity and the wavefunction of this electron is equally delocalized over these vanadium sites. Similarly, Boesman and Gills [23] investigated the paramagnetic centres in molybdenum-doped vanadium pentoxide crystals, and observed a hyperfine structure consisting of eight lines, indicating that in Mo-doped V_2O_5 a paramagnetic defect is formed in which the unpaired spin interacts with only one vanadium nucleus. Horvath *et al.* [24] reported that in vanadium phosphate glasses no hyperfine structure was observed due to spin–spin interaction. In contrast, Livage *et al.* [25] observed a hyperfine structure typical of a 3d electron localized on a single ^{51}V nucleus in the ESR spectra of vanadium phosphate glasses at low temperature. They also found that with increase in temperature, the broadening of hyperfine structure lines almost disappeared at room temperature.

Nicula *et al.* [26] studied the magnetic behaviour of xV_2O_5–$(100 - x)\%$ As_2O_3 glass and reported a change in the line width of ESR spectra due to coupling between V^{3+}–V^{4+} and V^{4+}–V^{4+} ions at different compositions. Friebele *et al.* [27] and Nicula *et al.* [26] suggested that the antiferromagnetic coupling between reduced vanadium ions (V^{4+}, V^{3+}, V^{2+}) in vanadate glasses reduces the concentration of V^{4+} ions. Friebele *et al.* [27] further noted that as the concentration of V_2O_5 in the vanadate glasses increases the concentration of V^{4+} ions decreases. Singh [4] recorded a weakly resolved hyperfine structure due to V^{4+} ions for low concentration of Fe_2O_3 in TeO_2–V_2O_5–Fe_2O_3 glasses at room temperature, whereas for higher concentration of Fe_2O_3 (3 mol %), the hyperfine structure of V^{4+} ions completely disappeared due to exchange interaction between V^{4+} ions and Fe^{3+} ions. Horvath and Szorenyi [28] reported a hyperfine structure of vanadium phosphate glasses under a low concentration of V^{4+} ions. They also suggested that the nearer the V^{4+} ions, the stronger was the dipolar interaction between V^{4+} ions. For a high content of V^{4+} ions, the hyperfine structure collapsed, indicating a stronger dipolar interaction than the nuclear hyperfine interaction. Kawamoto *et al.* [29] proposed the existence of a weak antiferromagnetic interaction between V^{4+} ions in the vanadium–bronze–vanadate (V_2O_5–V_2O_5–$Ba_{1/2}Zn_{1/2}O$) glasses. Harper and McMillan [30] observed a single line in the ESR spectra of V_2O_5–P_2O_5 glasses. Khawaja *et al.* [31] reported the ESR spectrum of V_2O_5–GeO_2 glasses to be typical for a 3d electron localized on a single ^{51}V nucleus. On annealing the sample, they observed the hyperfine lines to coalesce to a single line due to exchange interaction resulting from an increase in the concentration of V^{4+} ions.

So the ESR spectra of simple V_2O_5 and of samples mixed with other oxides are still a matter of debate. We have investigated the ESR spectra of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 thin films.

2. Experimental procedure

The samples of co-evaporated V_2O_5/B_2O_3 thin films of different compositions and constant thickness (≈ 300 nm) were deposited from analytical reagent grade materials on to a pre-cleaned silica 3 × 1 cm substrate fused on to two silica glass rods of 4 and 6 cm lengths, to fit the ESR spectrometer. The Speedivac Coating Unit model 19A/122 at a pressure of the order of 1.33×10^{-4} Pa was used for the co-evaporation of oxides following the technique which has already been established and described by Hogarth and Wright [32]. Vanadium pentoxide and boric oxide were evaporated from covered boats of molybdenum and tungsten, respectively. The evaporation parameters such as composition and thickness of the films were monitored by means of a quartz crystal monitoring system which was calibrated for each material. The total thickness of co-evaporated oxide thin films was measured by multiple beam interferometry, making use of Fizeau fringes of equal thickness. The ESR measurements were made at room temperature using a Varian E3-EPR spectrometer working at X-band at the same modulation amplitude, time constant and magnetic field scan for each sample. The amplifier sensitivity was changed for some samples to have a measurable signal trace. The spectrometer was calibrated in absolute spins cm^{-3} using ammonium vanadyl oxalate crystal of known spin concentration contained in a pyrex cell. The measurements were made for the same magnetic field of 3400 G and at a microwave frequency of 9.3 GHz for all samples. In order to avoid the hygroscopic effect, the ESR spectra were recorded soon after preparing the samples.

3. Results and discussion

The ESR spectra for different compositions of co-evaporated V_2O_5/B_2O_3 thin films can be seen in Fig. 1. The films showed a poorly resolved hyperfine structure for lower molar content of B_2O_3, whereas for higher content of B_2O_3 well-defined spectra were recorded. The co-evaporated V_2O_5/B_2O_3 films with molar content of B_2O_3 of 40% and above showed very well resolved hyperfine spectrum consisting of eight lines. We can explain this behaviour of our samples in the following manner.

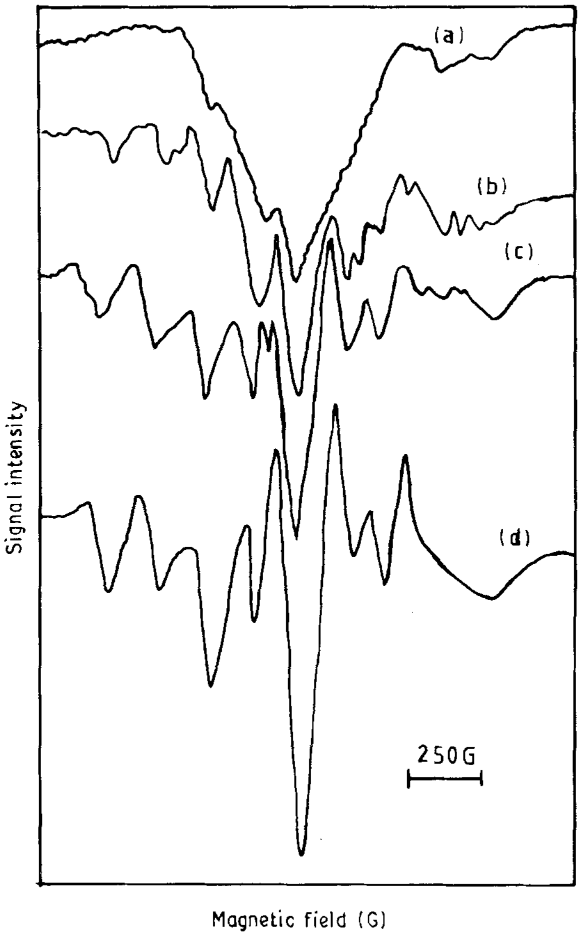

Figure 1 ESR spectra of co-evaporated V_2O_5/B_2O_3 ($\approx$ 300 nm) thin films of different compositions. (a) Simple V_2O_5, (b) 90 mol % V_2O_5, (c) 80 mol % V_2O_5, (d) 40 mol % V_2O_5.

Vanadium pentoxide is a non-stoichiometric compound in which oxygen deficiency is compensated by the reduction of some vanadium ions to a lower oxidation state, mostly V^{4+} with the $3d^1$ configuration which is paramagnetic and responsible for the ESR signal. We attribute the ESR signal in the co-evaporated films to the presence of V^{4+} ions, which has already been suggested in our investigation of the electrical and optical properties of co-evaporated V_2O_5/B_2O_3 thin films [33–35].

The nucleus of vanadium ^{51}V has a magnetic spin ($I = 7/2$). The spin of an unpaired electron of the V^{4+} ion can interact with the nuclear magnetic spin to give a hyperfine structure. The total number of lines in the hyperfine spectrum is given by $(2I + 1)$ where I is the magnetic spin of the nucleus. In this way if one unpaired electron interacts with one nucleus, then the total number of lines in the hyperfine structure should be eight, which we observed in the present case.

Friebele [9] suggested that the weak magnetic behaviour of vanadium phosphate glasses is due to the antiferromagnetic coupling of V^{3+}–V^{3+} and V^{4+}–V^{4+} ions. He also proposed that this type of antiferromagnetic coupling occurs predominantly between V^{4+} ions. Goodenough [36] reported a direct cation–cation interaction between transition metal ions. Such interactions are induced by the overlap of partially filled d orbitals of neighbouring transition metal ions. He further suggested that as the cation–cation separation is increased there is an abrupt transition in such reactions. Abe and Shimada [37] while studying the magnetic absorption of copper acetate, reported that two Cu^+ ions interact strongly to give the resultant spin $s = 1$ which is diamagnetic in character.

The low intensity of ESR signal in our case for the low concentration of B_2O_3 in the co-evaporated V_2O_5/B_2O_3 films can be attributed to the antiferromagnetic coupling of V^{4+}–V^{4+} ions. For the low concentration of B_2O_3, due to a low degree of disorder of the co-evaporated V_2O_5/B_2O_3 films, the separation between V^{4+}–V^{4+} ions is comparatively small. Thus the probability of interferromagnetic interaction between these ions will be higher and will result in a decrease of the effective concentration of V^{4+} ions. The observation made by Landsberger and Bray [38], that for higher concentration of V_2O_5 in vanadium phosphate glasses the concentration of V^{4+} ions is less, can also be attributed to similar type of behaviour. As we go on increasing the content of B_2O_3, the co-evaporated V_2O_5/B_2O_3 films will be more disordered because of the glass forming character of B_2O_3. Under these conditions the separation between V^{4+}–V^{4+} ions may increase and consequently the interaction between V^{4+} ions will decrease as a result of less antiferromagnetic coupling. The effective concentration of V^{4+} ions and hence the intensity of the ESR signal will increase as confirmed by our experimental results in Fig. 1.

This type of behaviour of our films is consistent with that reported by other authors [27, 28, 30, 39] that amorphous V_2O_5 films exhibit a well-resolved hyperfine structure as compared to crystalline V_2O_5.

As reported by Richtmeyer *et al.* [40], the linewidth of the hyperfine structure of V_2O_5 depends upon the lifetime of the V^{4+} ion. The unpaired electron is not always localized on a single particular ^{51}V nucleus but it moves from one to another following a hopping process, a property responsible for the semiconducting properties of transition metal oxides.

We suppose that Δt is the lifetime during which the $3d^1$ unpaired electron is localized on a single particular ^{51}V nucleus. Then according to the Hesienberg uncertainty principle we have $\Delta E.\ \Delta t \approx h$ where ΔE is the uncertainty in the energy of the state. So for shorter values of Δt, the values of ΔE will be larger. It should be remembered that ΔE is directly related to the width of lines of the hyperfine spectra. Hence a narrow line would be observed in the case of a transition between two well-defined (well separated) energy states in contrast to the transition between poorly-defined energy states which would give a broad line.

So we suppose that under the lower molar content of B_2O_3 in co-evaporated V_2O_5/B_2O_3 films, the disorder will be less and consequently the lifetime of a particular V^{4+} ion will be less, thus resulting in increased line broadening and the spectrum will be poorly resolved. On the other hand if we go on increasing the molar content of B_2O_3 in the co-evaporated V_2O_5/B_2O_3 films, the degree of disorder will increase as a result of the glass forming character of B_2O_3 and an Anderson localization of charge carriers on V^{4+} ions will occur. This phenomenon will increase the lifetime of a particular V^{4+} ion so ΔE will decrease, and consequently the width of the lines in the hyperfine spectra of the films will decrease so that they do not overlap and we get well resolved hyperfine spectra. This type of behaviour of our films is consistent with the studies of optical and electrical conduction characteristics of co-evaporated V_2O_5/B_2O_3 films reported elsewhere [33–35].

The presence of eight lines in the hyperfine spectra of co-evaporated films is attributed to the fact that the unpaired electron is localized over a single ^{51}V nucleus. So we propose that the hyperfine structure of co-evaporated films is a result of the interaction between the unpaired spin of a V^{4+} ion and the spin of a vanadium nucleus and that the unpaired electron is localized over a single vanadium ion.

4. Conclusion

The low intensity of the ESR signal for the higher concentration of V_2O_5 in co-evaporated V_2O_5/B_2O_3 films has been attributed to the less effective concentration of V^{4+} paramagnetic centres due to antiferromagnetic coupling of V^{4+} ions as a result of having less disorder. The well defined hyperfine structure at higher molar content of B_2O_3 in the co-evaporated V_2O_5/B_2O_3 films has been related to the higher lifetime of a particular V^{4+} ion due to Anderson localization of charge on that particular V^{4+} ion. The presence of eight hyperfine lines indicates that the unpaired electron is localized on a single ^{51}V nucleus.

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