CHARACTERIZATION OF AMORPHOUS VANADIUM PENTOXIDE THIN FILMS PREPARED BY CHEMICAL VAPOUR DEPOSITION (CVD) AND VACUUM DEPOSITION

By

L. MICHAILOVITS, K. BALI, T. SZÖRÉNYI and I. HEVESI

RESEARCH GROUP ON LUMINESCENCE AND SEMICONDUCTORS, HUNGARIAN
ACADEMY OF SCIENCES, SZEGED, HUNGARY

Amorphous vanadium pentoxide thin films were prepared by CVD of $VOCl_3$ with H_2O at room temperature and by vacuum deposition. The stoichiometry was estimated from quantitative EPR measurements. The amorphous to crystalline transition temperatures, 453—463 K for vacuum deposited films and 523 ± 10 K for films prepared by CVD, were determined by DTA, polarization microscopy and electrical conductivity measurements. The structural changes were monitored by electron microscopy and EPR.

Introduction

Two methods are known to obtain pure amorphous vanadium pentoxide (V_2O_5), splat-cooling [1, 2] and vacuum deposition [3—6]. Both methods involve the melting of the material. At high temperatures the melted V_2O_5 loses oxygen resulting in a non-stoichiometric oxide. The deviation from the stoichiometry depends on the temperature. An attempt to prepare amorphous V_2O_5 thin films of probably lower V^{4+} content (sub-melting-point vacuum evaporation) was reported by COLTON [7].

Although relatively high temperatures are needed to obtain single crystals of good quality chemical vapour deposition proved to be a convenient method for growing crystalline vanadium oxides [8—10]. The great advantage of this method is that the stoichiometry can easily be controlled. Since the decomposition of vanadium oxychloride ($VOCl_3$) vapour with H_2O vapour is a strongly exothermic process, the reaction takes place even at room temperature according to the equation

$$2VOCl_3 + 3H_2O \rightarrow V_2O_5 + 6HCl, \tag{1}$$
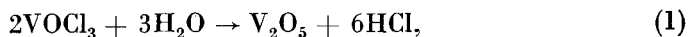
which suggests that CVD at room temperature might yield non-crystalline V_2O_5 of possibly very low V^{4+} content.

In this paper we report the successful preparation of amorphous vanadium pentoxide thin films by CVD and compare the properties of the films prepared by this method and vacuum deposition.

Experimental

The starting material for vacuum deposition was V_2O_5 powder (REANAL, Hungary, purum grade). The temperature of the electrically heated molybdenum boats, as determined by an optical pyrometer, was 1670 K. The substrates were held at room temperature under high vacuum ($< 1 \times 10^{-3}$ Pa). Film thickness varied between $0.2-0.8$ μm at deposition rates of $3-5$ nm/s and a boat to substrate distance of 0.1 m.

To apply the CVD method $VOCl_3$ vapour (FLUKA, Switzerland) and H_2O both thermostated at $303-333$ K and $295-298$ K, respectively, were introduced into the quartz reaction tube by high purity N_2 or O_2 carrier gas, dried in an LN_2 cooled baffle.

Quartz and optical glass plates, polyethylene and mylar films were used as substrate materials. For electron microscopic studies the films were deposited onto platinum grids covered by a collodion and a vapour deposited SiO_x layer.

The electron micrographs were taken with a JEM 100-U (JEOL) microscope; for EPR measurements a JES—PE—1X (JEOL) X-band spectrometer was used; the IR spectra were recorded with an UNICAM SP 200 spectrophotometer. Electrical resistivity was measured by two point technique using evaporated platinum electrodes. Density data were calculated from measured weight/volume ratios. The thicknesses of the films were determined by optical interference method.

Results and discussion

Thin films prepared by both methods were originally yellow and uniform in appearance. With optical microscopy we were unable to distinguish them, but TEM pictures clearly showed that vacuum deposited samples were more homogeneous than those prepared by CVD.

LIVAGE and his coworkers proposed a very simple method to distinguish between crystalline and amorphous V_2O_5. They pointed out that the crystalline form cannot be dissolved in water while the amorphous form readily dissolves [1, 2]. Our films easily dissolved in water yielding a yellow solution with pH $\sim$ 2. The electron microscopic studies proved unambiguously that the films were amorphous (Fig. 1a).

The density of the samples varied from 2.7 gcm^{-3} to 3.1 gcm^{-3}. The large spread is possibly due to uncertainties in weight and thickness measurements.

The variation of electrical conductivity with temperature of an initially amorphous film prepared by vacuum evaporation is shown in Fig. 2. The
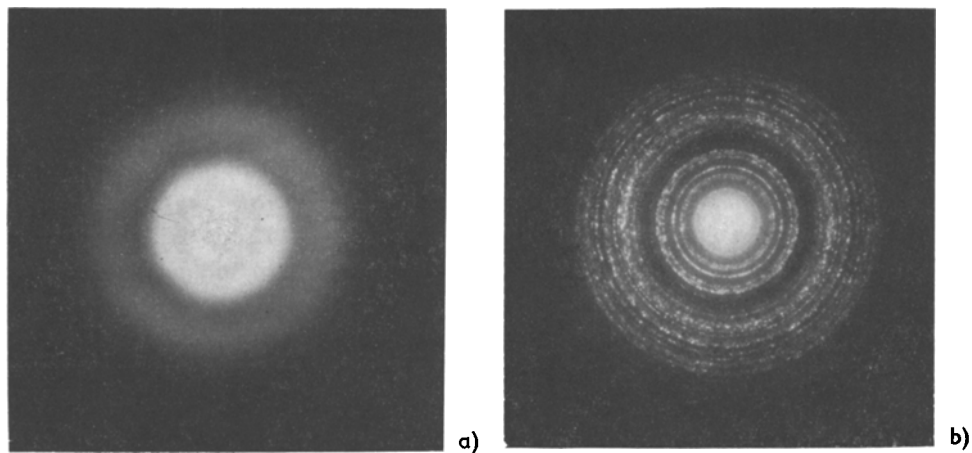
Fig. 1. Selected area electron diffraction pattern of an as-deposited film (a), and of the same film after heat treatment (b)
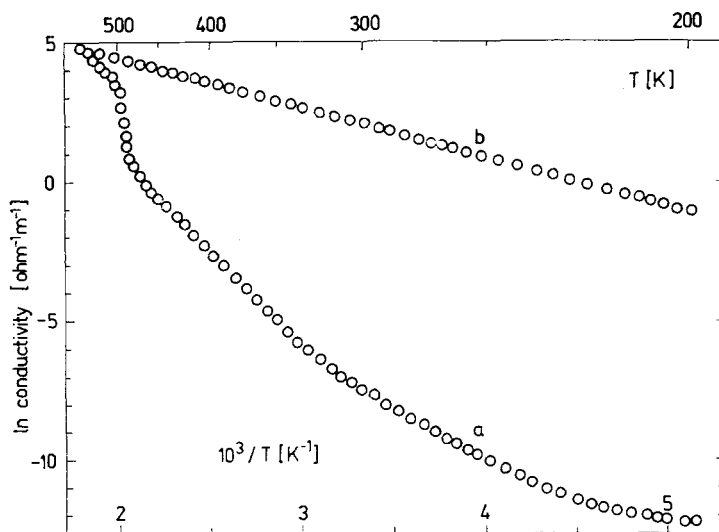

Fig. 2. Temperature dependence of the conductivity, measured on a vacuum deposited film

temperature dependence of conductivity in the amorphous phase (curve a) is consistent with the polaron model for conduction [11]. Conductivity values (measured on 7 different samples at 25 °C) ranged from 2×10^{-4} to 1×10^{-3} ohm^{-1}m^{-1} with a mean value of 6×10^{-4} ohm^{-1}m^{-1}. The high temperature activation energies were determined in the 300—450 K range. The mean value of 0.62 eV is surprisingly high as compared to data reported by ALLERSMA

et al (0.29—0.39 eV) [4]. The amorphous to crystalline transition temperatures (defined by the temperature at which the conductivity suddenly increases) of the vacuum evaporated samples were found between 453 and 463 K, in agreement with our own results obtained by DTA and polarization microscopy, and those of [1, 2]. The conductivity of the crystallized material (curve b in Fig. 2) can be described by the equation

$$\sigma = \sigma_0 \exp(-E/kT) \tag{2}$$

with $E = 0.14$ eV which is close to the value reported for single crystals and polycrystalline material [3, 4]. Conductivity values of 6 $ohm^{-1}m^{-1}$ were measured at room temperature. The polycrystalline material was identified as orthorhombic V_2O_5 (ASTM 9—387) (Fig. 1b). The density of the polycrystalline films increased by 25% as compared to that of the amorphous samples.

The crystallization temperature of the CVD films was found, as determined by the same methods, 520 ± 10 K. For hydrated amorphous V_2O_5 transition temperatures between 570 and 600 K were reported [12], suggesting that the higher transition temperature observed might be due to the presence of water. Indeed, the DTA curves showed a weak endotherm signal at about 370 K. In the IR spectra two bands at 1610 and 3500 cm^{-1} could be identified beside the characteristic peaks at 650, 840 and 1015 cm^{-1}. These results proved that the films prepared by CVD contain loosely bound water.

The lineshape of the EPR spectra is of diagnostic value for distinguishing between the amorphous and crystalline forms and also for estimating the V^{4+}
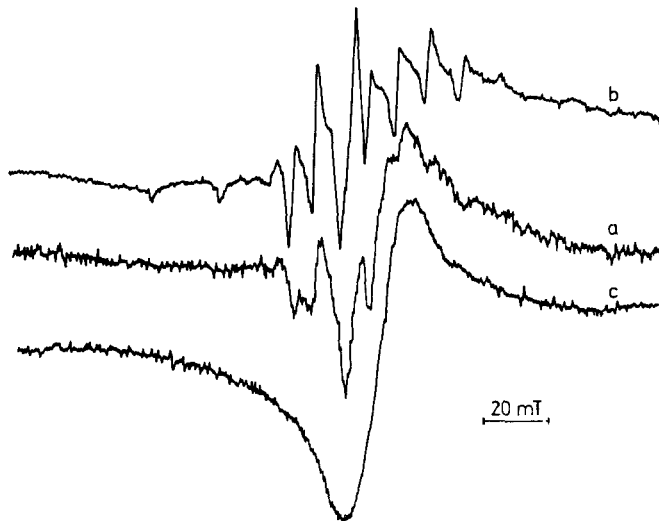

Fig. 3. EPR spectra of an as-deposited CVD film, recorded at 300 K (a) and 100 K (b); spectrum of the film after heat treatment, recorded at 300 K (c)

content. The amorphous form of low V^{4+} content exhibits a well resolved hyperfine pattern at room temperature unlike crystallized V_2O_5 [1, 2, 13]. EPR spectra of a CVD film are shown in Fig. 3. The spectra labelled with a and b are characteristic of the amorphous phase with low V^{4+} content; while the spectrum recorded after a heat treatment at 570 K for 3 hours in oxygen atmosphere (curve c) is characteristic of the crystalline phase. The room temperature EPR spectra of films prepared by vacuum deposition exhibited no hfs indicating the presence of much more V^{4+}. Quantitative EPR measurements using $CuSO_4 \cdot 5H_2O$ standard revealed that the films prepared by CVD contained only $1-2\%$ V^{4+}, while the V^{4+} content of the films obtained by vacuum deposition was $7-8\%$

Summing up it may be stated that the amorphous films obtained by vacuum deposition are of very good homogeneity but exhibit large deviation from the stoichiometry; while CVD is appropriate to produce near stoichiometric amorphous vanadium pentoxide thin films.

REFERENCES

1. J. LIVAGE and R. COLLONGUES, Mater. Sci. and Eng., 23, 297, 1976.
2. L. RIVOALEN, A. REVCOLEVSCHI, J. LIVAGE and R. COLLONGUES, J. Non-Crystalline Solids, 21, 171, 1976.
3. T. N. KENNEDY, R. HAKIM and J. D. MACKENZIE, Mater. Res. Bull., 2, 193, 1967.
4. T. ALLERSMA, R. HAKIM, T. N. KENNEDY and J. D. MACKENZIE, J. Chem. Phys., 46, 154, 1967.
5. E. F. RYANNEL', V. I. GAMAN and V. M. KALIGINA, Izv. VUZ Fiz., 2, 102, 1976.
6. E. F. RYANNEL', V. M. KALIGINA and V. I. GAMAN, Fiz. and Khim. Stekla, 2, 109, 1976.
7. R. J. COLTON, A. M. GUZMAN and J. W. RABALAIS, J. Appl. Phys., 49, 409, 1978.
8 H. TAKEI and S. KOIDE, J. Phys. Soc. Japan, 21, 1010, 1966.
9. H. TAKEI, Japan. J. Appl. Phys., 7, 827, 1968.
10. J. FAN and W. PAUL, Vide, 150, 232, 1970.
11. I. G. AUSTIN and E. S. GARBETT, in Electronic and Structural Properties of Amorphous Semiconductors, Academic Press, London, 1973.
12. M. MICHAUD, M. C. LEROY and J. LIVAGE, Mater. Res. Bull., 11, 1425, 1976.
13. A. KAHN, J. LIVAGE and R. COLLONGUES, Phys. Stat. Sol. a, 26, 175, 1974.