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Growth and characterization of vacuum-deposited polyvinylcarbazole (PVK) films

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The optical and infrared absorption spectra of polyvinylcarbazole (PVK) films deposited by vacuum evaporation show identical shape when compared with the corresponding spectra of solution-grown PVK films obtained by thermal evaporation of the solution of PVK and dichloromethane. This confirms the formation of PVK films on vacuum deposition. Electron spectroscopy for chemical analysis measurements indicate the presence of carbon and nitrogen in these films as expected from the structure of PVK. The scanning electron micrographs indicate that the surface of these vacuum-deposited films are quite smooth and remain so even after annealing them in the atmosphere at 373 K for 1 h.

1. Introduction

Polyvinylcarbazole (PVK) is an attractive polymer owing to its photoconductive properties. It has been used in xerographic systems. The Al/PVK/a-Se devices have been studied extensively [1–4]. In these systems the carriers are photogenerated in thin amorphous selenium upper layer of thickness ~ 1 μm – the so-called charge generation layer. Then these carriers are injected into a thicker ~ 10 μm layer of PVK – the so-called charge transporting layer. The aluminium electrode, is a blocking contact with PVK. Mort [2] has shown that the abrupt drop in the injection efficiency observed in the xerographic mode can arise from the trap-free surface-charge-perturbed currents in PVK. In general, and in the above devices in particular, the PVK films used are solution grown, i.e. they were prepared [1–7] from solutions of the polymer in solvents (dichloromethane, cyclohexane, toluene, chloroform, etc.). The thickness of the films is generally between 1 and 20 μm or more. However, it may be promising to obtain thin PVK films by other techniques, in order to try to increase the properties of PVK-based films. Recently, electrochemical preparation of PVK layers has been described [8].

In this paper we describe a simple so-called vacuum evaporation technique to deposit PVK films, which has some distinct advantages over the solution evaporation technique. For example, (i) this technique is quicker, because in solution evaporation the films have to be dried, and (ii) Al/PVK/a-Se type of devices may be obtained in a single run without breaking the vacuum, etc.. Such vacuum-deposited films of PVK have been characterized by optical absorption (infrared absorption, visible and near-ultraviolet absorption), photoelectron spectroscopy (XPS analysis), electron microscopy and electrical measurements.

2. Experimental procedure

The PVK films were obtained by evaporation of PVK powder under vacuum ~ 10^{-3} Pa from a molybdenum boat. This boat has a special configuration in order to avoid the calefaction of the PVK powder. The substrates were glass, silica slides, CaF_2 single crystals for IR measurements, or aluminium plates. During deposition the substrate temperature was 300 K. The films were annealed either *in situ* or under an argon or room atmosphere. The temperature was controlled by a copper–constantan thermocouple attached by silver paste to the surface of the sample. The substrates were chemically cleaned and then heated at 400 K for 1 h prior to deposition. Also prior to deposition the molybdenum boat was slowly heated for degassing the PVK powder. The evaporation rate and film thickness (0.05–20 μm) were measured *in situ* using the vibrating quartz method. The thickness of the films was controlled by interferometry. The optical measurements were carried out at room temperature for visible and near-ultraviolet domains using a Carry spectrophotometer. The optical density (OD) was measured at wavelengths from 2–0.3 nm. These optical measurements were carried out in the Laboratory of Crystalline Physics, Nantes, while infrared absorption spectra were carried out in the Laboratory of Ion Spectra Chemistry of Nantes, with a Fourier transform–infrared spectrometer. Electron spectroscopy for chemical analysis (ESCA) measurements were conducted with a Leybold spectrometer (University of Nantes, CNRS), and X-ray photoelectron spectroscopy (XPS) measurements were performed with a magnesium X-ray source (1253.6 eV) operating at 10 kV and 10 mA. The energy resolution was 1 eV at a pass energy of 50 eV for XPS. For insulating substrates, thin films were earthed using silver paste. The

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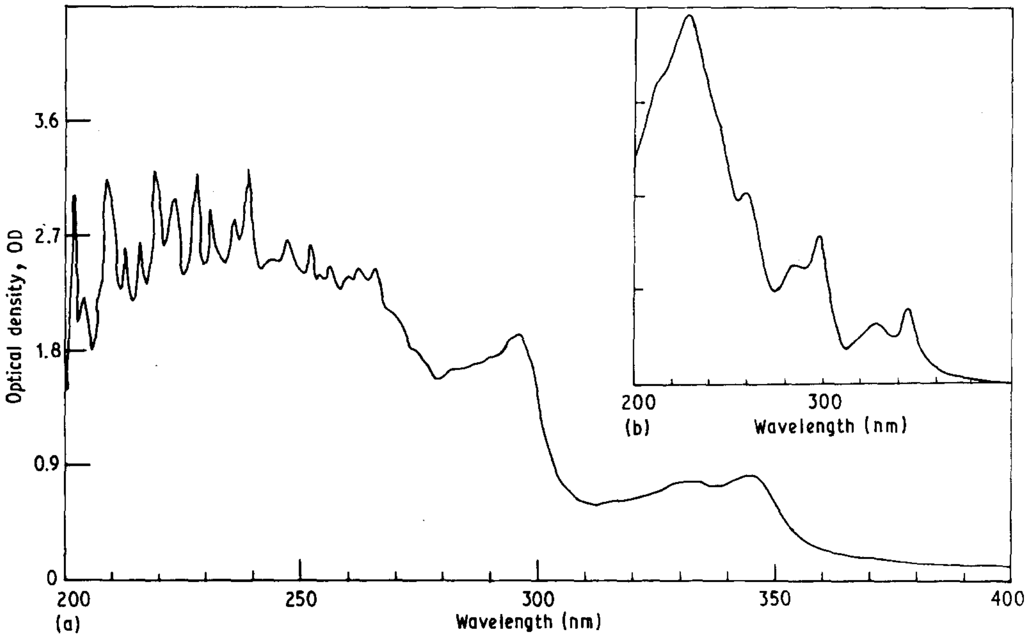

Figure 1 (a) Optical density (OD) (T = transmission coefficient) of a PVK evaporated thin film (thickness t = 100 nm, deposition rate 2 nm s^{-1}) (b) Typical optical spectrum of PVK.

surface of the films could be cleaned by argon ion etching. Sputtering was accomplished at pressures of less than 5×10^{-4} Pa, an emission current of 10 mA and a beam energy of 3 kV, using an ion gun. Observations of the surface topography were performed using a Jeol 6400 field-effect scanning electron microscope (SEM) in order to show the variation of morphology, if any, of the films, before and after annealing.

The I–V measurements were carried out with M/PVK/M sandwich structures. The metallic electrodes, M, were deposited by vacuum evaporation.

Measurements with gold electrodes in Au/PVK/Au sandwich structures were unsuccessful because the samples were short circuited, probably by gold diffusion during the upper electrode deposition; therefore, aluminium electrodes were used. The electrical measurements were carried out in the dark under room atmosphere. The electrical resistivity of the films was calculated from the resistance, which was derived from the measurement of I–V characteristics using the film thickness measured. The steady state value of the current was recorded with an electrometer.

3. Results and discussion

Fig. 1a shows a typical optical spectrum of a thin evaporated PVK film, and Fig. 1b shows the reference optical spectrum of PVK. The shapes of the curves are quite similar. The absorption is entirely in the ultraviolet region, with peaks situated around 260, 285, 295, 330 and 345 cm^{-1}. Below 250 cm^{-1}, the saturation of the OD is tied to the thickness of the film.

A reference infrared spectrum was obtained from PVK powder. In Fig. 2 the Fourier transform–infrared spectra show that PVK was unaffected by the vacuum deposition. Moreover, the infrared spectrum is similar to that which is given by Papez *et al.* [8] (Fig. 9b). Therefore, we can conclude that the polymer is not decomposed by heating during the evaporation.

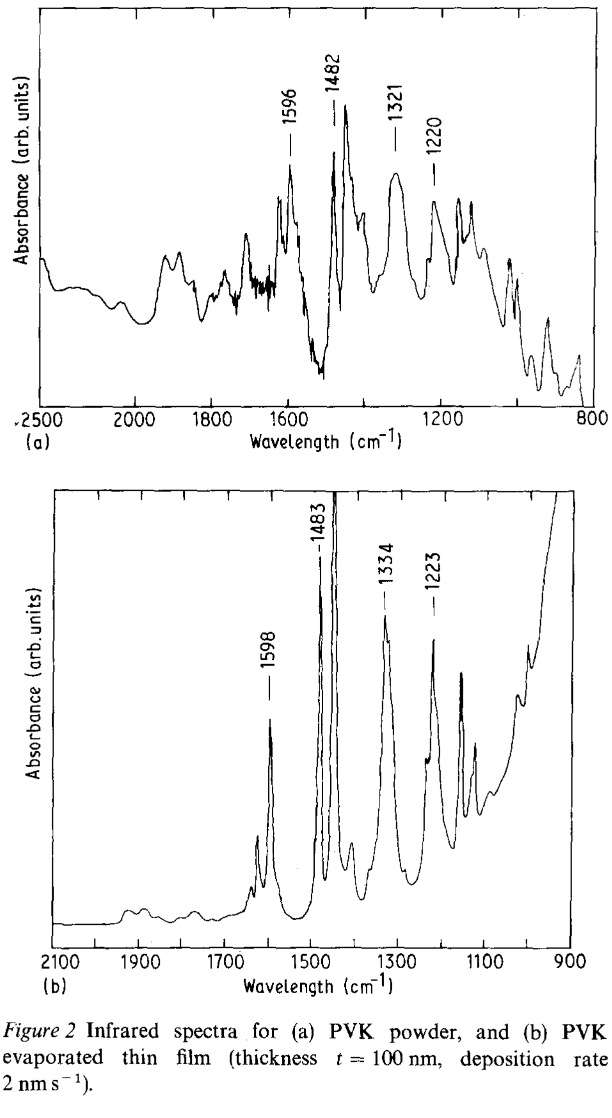

Figure 2 Infrared spectra for (a) PVK powder, and (b) PVK evaporated thin film (thickness t = 100 nm, deposition rate 2 nm s^{-1}).

The scanning electron micrographs in Fig. 3a–d show films of various thicknesses prepared by vacuum evaporation. The rate of evaporation was varied between 1 and 20 nm s^{-1}. When the rate of evaporation

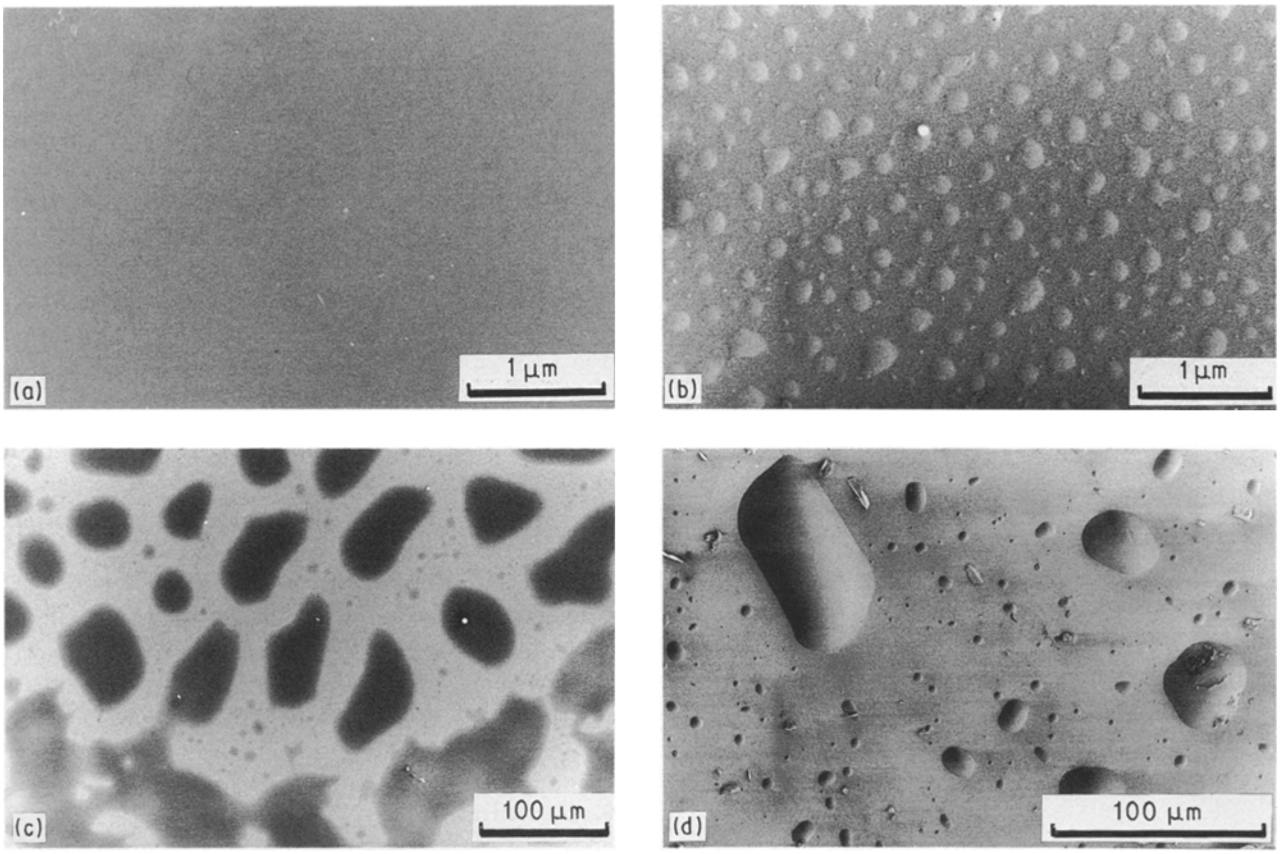

Figure 3 Scanning electron micrographs of PVK films prepared by vacuum evaporation at: (a) 4 nm s^{-1}, $t = 200$ nm, clean substrate; (b) 4 nm s^{-1}, $t = 200$ nm, unclean substrate; (c) 20 nm s^{-1}, $t = 200$ nm, clean substrate; (d) 20 nm s^{-1}, $t = 500$ nm, clean substrate.

was small, about 1–4 nm s^{-1}, the substrate was covered with a smooth, uniform PVK layer (Fig. 3a). At the same deposition rate, sometimes some hemispherical configurations began to appear on this layer (Fig. 3b); this may be attributed to the substrates being not clean enough. The size of these hemispherical configurations increases after annealing at 373 K for 1 h. This increase is greater when the annealing is monitored under room air atmosphere rather than under a nitrogen or argon atmosphere.

When the rate of deposition increases (20 nm s^{-1}), discontinuous thin films are obtained even when the films are 200 nm thick (Fig. 3c). However, at the same deposition rate, the films become continuous when they are thicker (500 nm) yet the surface of the films is not smooth (Fig. 3d). Therefore, when deposited at a slow rate, the PVK films initially grow uniformly, forming a homogeneous, compact layer all over the substrate surface (Fig. 3a). When deposited on a substrate having a small amount of dust on the surface (Fig. 3b) the film is rough with the formation of globular structures which may correspond to the local dust. As PVK is very soft, it is extremely sensitive to the surface state of the substrate. When the rate of deposition is faster, the film grows irregularly with heap formation, before the film becomes continuous. This heap formation is maximized by the roughness of the surface of the films when they become continuous.

Fig. 4 shows the XPS survey spectrum of a PVK film after 1 min sputtering. It can be seen that only carbon and nitrogen peaks are visible as expected from the structure of PVK. In Fig. 5 the C 1s, N 1s and O 1s region of the XPS spectra of a thin evaporated film deposited on aluminium substrate and of a bare aluminium substrate are presented. Before sputtering we can see that the C 1s and N 1s peaks of the PVK film (Fig. 5, curves 3) are very large and anisotropic. They correspond to two peak structures. By comparison with spectra obtained on the aluminium substrate before sputtering (Fig. 5, curves 1), the most intense peak (286 and 401 eV for C 1s and N 1s, respectively) may be attributed to the air contamination of the sample surface. After sputtering, the C 1s and N 1s peaks disappear in the aluminium substrate spectrum (Fig. 5, curve 2), while in the PVK film, the C 1S and N 1s peaks situated at 286 and 401 eV, respectively, decrease dramatically (Fig. 5, curve 4) which

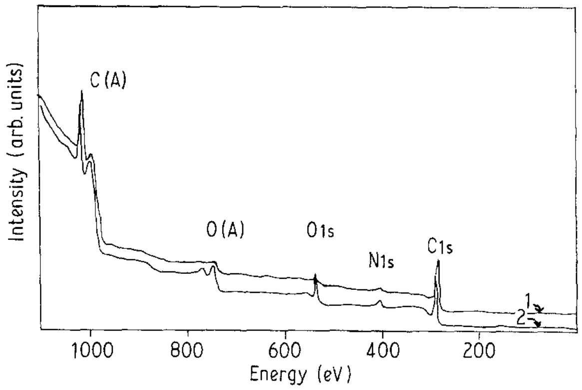

Figure 4 XPS survey spectrum of a PVK film (1) after 1 min sputtering, (2) before sputtering.

confirms that they may be attributed to surface contamination. The C 1s and N 1s peaks situated at 284.5 and 399.5 eV, present after sputtering of the PVK films, correspond to the shoulder of the C 1s and N 1s peaks before sputtering. These peaks may be attributed to the carbon and the nitrogen bound in the polymeric structure of the PVK. With increasing sputtering time of the films, the binding energies of the C 1s and N 1s peaks are stable (284.5 and 399.5 eV, respectively) which confirms the depositon of PVK films. Further, after sputtering, the nitrogen peak location (399.5 eV) confirms the covalent nature of the nitrogen bonding. The absence of oxygen (Fig. 4) after 1 min sputtering, and the C 1s peak location, confirms that the carbon is not oxidized and that PVK is not dearranged during evaporation. The oxygen spectra (Fig. 5, curves 3 and 4) show that the films are not polluted by oxygen.

The *I–V* characteristics were ohmic in the field range investigated and the electrical resistivity calculated from the slope of these characteristics was about $10^{12}\,\Omega$cm. This value is in good agreement with that obtained by Papez *et al.* [8] on electrochemically deposited PVK layers.

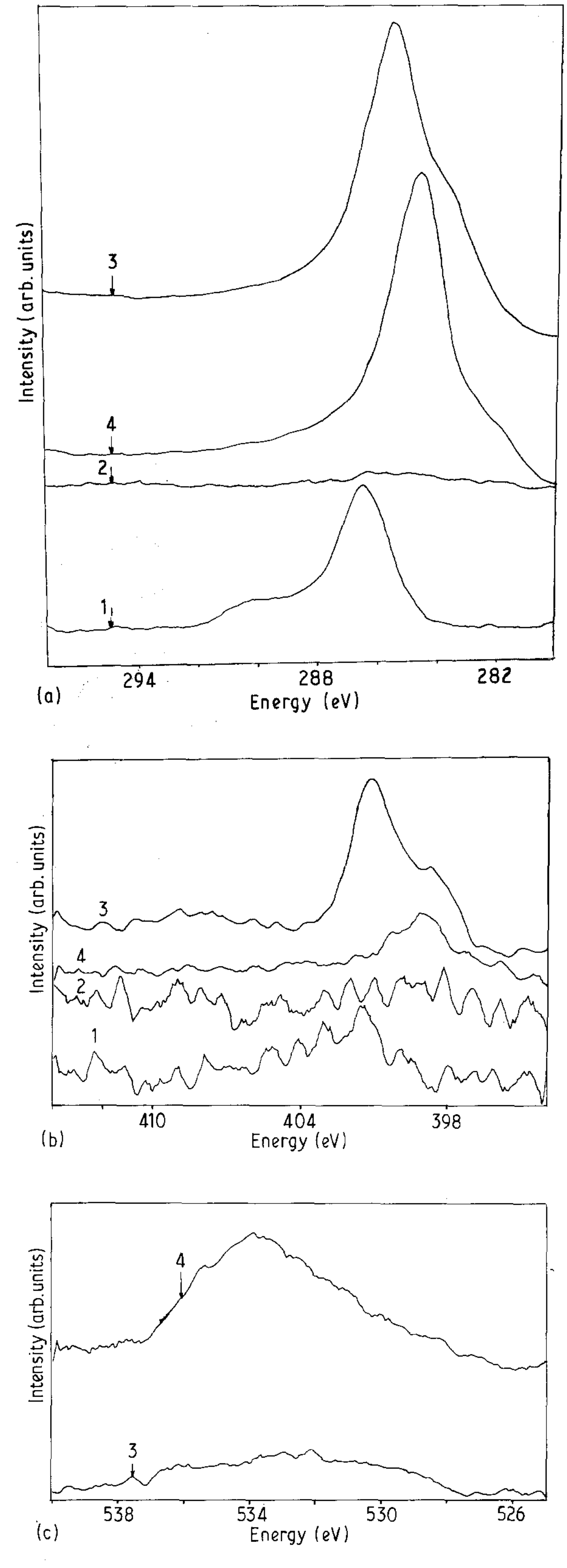

Figure 5 XPS spectra of PVK evaporated thin films: (a) C 1s, (b) N 1s, (c) O 1s. Curve 1, reference aluminium substrate; Curve 2, reference aluminium substrate after 3 min sputtering; Curve 3, PVK evaporated thin films; Curve 4, PVK evaporated thin films after 1 min sputtering.

4. Conclusion

Continuous, smooth PVK films have been obtained with a thickness ranging between 0.05 and 20 μm by vacuum evaporation at a rate of 1–4 nm s^{-1}. The optical spectra (visible, near ultraviolet and infrared) and the XPS analysis confirm that the PVK has not been decomposed during vacuum evaporation. The surface topology of the films is very sensitive to the deposition rate and to the surface of the substrate: the surface of the substrate has to be very clean and the optimum deposition rate is about 1–4 nm s^{-1} in order to obtain smooth, continuous films.

References

1. C. CHEN and J. MORT, *J. Appl. Phys.* **43** (1972) 1164
2. J. MORT, *Phys. Rev.* **5** (1972) 3329
3. P. M. BORSENBERGER and N. MEY, *J. Non-Cryst. Solidi* **28** (1978) 305.
4. B. REIMER and H. BASSLER, *Phys. Status Solidi* (*a*) **51** (1979) 445.
5. P. J. ROUCROFT and K. T. TAKAHASHI, *J. Non-Cryst. Solidi* **17** (1975) 71.
6. G. PFISTER and C. H. GRIFFITHS, *Phys. Rev. Lett.* **40** (1978) 659.
7. A. SZYMANSKI and M. M. LABES, *J. Chem. Phys.* **50** (1969) 3568.
8. V. PAPEZ, O. INGANAS, V. CIMROVA and S. NESPUREK, *J. Electroanal. Chem.* **282** (1990) 123.

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