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Chemico–Physical Characterization of Quinizarin Thin Films Deposited by Evaporation

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Quinizarin (1,4-DHAQ) thin films deposited under vacuum were investigated by IR absorption, X-ray diffraction, nuclear magnetic resonance (NMR), optical absorption, electron spectroscopy for chemical analysis elemental analysis (XPS), and scanning electron microscopy and melting point measurements. It was found that amorphous quinizarin thin films are obtained. IR absorption spectra, ion mass spectroscopy, and NMR spectra show that there is no decomposition during the deposition of the film, the quinizarin powder being sublimated under vacuum from a tantalum boat sustained at T = 418 K. In addition, elemental analysis and melting point measurements demonstrate that the deposition process is also a purifying process of the quinizarin. SEM microphotographs show that continuous, smooth thin films may be obtained when they are deposited at a sufficiently slow rate. XPS analysis shows that, after decomposition of the peak spectra, the O_{1s} peak is composed of two different components corresponding to the oxygen bonded in the carbonyl and the hydroxyl groups. In the case of the C_{1s} peak, the main component corresponds to the carbon of the cycle, while it was not possible to discriminate between the carbonyl and hydroxyl bonds, perhaps because of the hydrogen bond between these two groups. The presence of an absorption band around 480 nm in the optical absorption confirms the hydrogen bond between the hydroxyl and carboxyl in the 1,4-DHAQ. Optical absorption of an Ag/DHAQ structure shows that a complex may be obtained by annealing. © 1993 Academic Press, Inc.

Introduction

The search for a reversible optical recording organic material is a long process. Dyes were selected from the known classes of thermally and photochemically stable dyes such as the anthraquinones, the phthalocyanines, and some of the squaryliums. They are known to undergo phase changes, but they appear to be nonreversible in the last two families, therefore anthraquinone dyes were studied. Some of them present a reversible phase change, but the erasure time is long and the reproducibility cycle poor (*1*).

Another field may be investigated. It has been shown by Poehler, Potember, and coworkers (*2–7*) that the effect of an applied optical field in the Ag TCNQ charge transfer salt induces a phase transition. This results in the formation of a nonstoichiometric complex salt containing neutral TCNQ and a change in the layers' optical properties. However, the switching is quite slow and the reproducibility poor.

Since anthraquinones present good ther-

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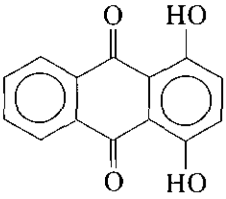
mal, photochemical stability and could form charge transfer salts, we further investigated some anthraquinone derivatives and their complex salts in our laboratory (*8–11*). Here, quinizarin has been studied.

The quinizarin, 1,4-dihydroxyanthraquinone, (1,4-DHAQ) (inset Fig. 3) has been largely studied recently because of its properties in photochemical hole burning (PHB) which may be interesting for high density memories improvement (*12–16*). At the moment this phenomenon still exits at a temperature too low for memory applications. Nevertheless, quinizarin thin films properties are now being investigated in our laboratory and the results obtained from Ag/DHAQ structures are very promising.



1.4 DHAQ

II. Experimental Procedures

Films of 1,4-Dihydroxyanthraquinone (quinizarin) with thickness ranging from 500 nm to 5000 nm were deposited under dynamic vacuum (base pressure 10^{-4} Pa) by sublimation of quinizarin powder (Aldrich powder purity better than 96%) from a tantalum boat. The substrates were polished glass, mica, and silica stainless steel slides. The stainless steel substrates were used for ESCA analysis. During deposition the substrate temperature was room temperature. The films were annealed *in situ*, the substrate temperature being controlled by a copper–constantan thermocouple attached by silver paste to the surface of the sample. The temperature of the tantalum boat was also controlled by a thermocouple attached to the boat. The evaporation rate and the film thickness were measured *in situ* by the vibrating quartz method.

Quinizarin films were identified by IR absorption, ion mass spectroscopy, Nuclear Magnetic Resonance (NMR), and by elemental analysis, while the purity of the films was checked by measuring their melting point.

X-ray photoelectron spectroscopy measurements (XPS) 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 grounded with silver paste. The surface of each film was 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. XPS measurements were carried out in Nantes with a Leybold Spectrometer (University of Nantes, CNRS).

Observations of the surface topology were performed using a JEOL 6400 F field effect scanning electron miroscope (SEM). Optical measurements were carried out with a Cary spectrophotometer from 2 to 0.2 μm. The thicknesses were checked by a mechanical stylus profilometer in order to permit the control of the surface topology of the thin films. This method requires the presence of a step between the substrate surface and the film surface so that the stylus is vertically displaced as it traverses the sample. Such steps can be produced by masking portions of the substrate during deposition. Masking requires that the mask is in close contact with the substrate and is very thin in order to avoid shadowing and accumulation of material near the step edge. Therefore a cover glass was used as a mask.

For elemental analyses, IR absorption, NMR and melting point studies, the quinizarin films were scratched from the substrate. Infrared spectra were obtained in KBr pellets in a FITR spectrometer. Band positions are expressed in wave numbers (cm^{-1}) the pellets were obtained by mixing scratched quinizarin powder with KBr powder.^{1}H-NMR (100 MHz) spectra were recorded on a Varian XL-100 spectrometer and on a Bruker WM 250 MHz machine.

TMS was used as internal standard and $CDCl_3$ as a solvent. Ion mass spectroscopy was performed on powders and thin films. Elemental analyses were performed in a CHN Heraeus Mikrostandart analyzer. Melting points were measured on a Kofler hot-stage apparatus and were uncorrected.

In order to obtain metallic complex with Ag, silver thin films were deposited onto the DHAQ thin films without breaking the vacuum between the two evaporations. The thickness ratio $t_{Ag}/t_{1,4\text{-DHAQ}}$ is 0.13.

Results and Discussion

Reference spectra (IR, XPS, optical absorption, . . .) were obtained from quinizarin powder. In Fig. 1 the Fourier transform IR spectra show that quinizarin was unaffected by the vacuum deposition. Moreover, the IR spectrum is identical to that which is given by the handbook (*17*). The C=O stretching region in the IR spectra is located around 1630 cm^{-1} which is smaller than the 1678 cm^{-1} measured in the case of anthraquinone. This agrees well with an hydrogen bonding of the carbonyl group with the hydroxyl function. In quinizarin such an interaction is well known to decrease the π electronic density of the carbonyl system and thus lower the absorption frequency of this vibration. The other bonds are indicated Fig. 1a in the light of preceeding studies (*18, 19*).

After deposition, X-ray diffraction analyses show that the films were amorphous. The films cannot be crystallized, even under atmospheric pressure, because during an annealing at 370 K either the film escapes from the substrate or it is still amorphous after the annealing. The surface roughness of the film has been checked by a stylus. The surface of the films appears to be quite smooth.

The scanning electron micrographs for the films are presented in Fig. 2. The variations in morphology have been studied with the deposition rate. We can see that the films become more continuous and more homogeneous when the deposition rate is between 0.2 and 0.3 nm/s.

The evaporation begins when the temperature is around 390 K and the evaporation rate stabilizes at 0.3 nm/s when the temperature of the boat reaches 418 K, which is far smaller than the decomposition temperature of the quinizarin (466 K).

^{1}H-NMR spectra were recorded for the Aldrich powder, the Aldrich powder after purification by recrystallization in acetic-acid (CH_3COOH), and the powder obtained from quinizarin sublimated thin films. All the spectra were identical (Fig. 3). Moreover, these spectra are the same as those which are given in the handbook (*20*). The chemical shifts measured from TMS are $\delta_{H_a} = 7.40$, $\delta_{H_c} = 7.90$, $\delta_{H_b} = 8.46$, and $\delta_{OH} = 12.90$ ppm. These results are consistent with the electronic repartition in the quinizarin (Fig. 3). The distribution of intensities between the peaks is 1 : 1 : 1 : 1 which are the values expected from the chemical formulae of the quinizarin.

In Fig. 4 we can see the positive ion mass spectrum of the powder and the thin film. The spectra are similar and they are identical to the reference handbook data. However, the quinizarin powder and film show small peaks at about 274 which is above the parent peak of the quinizarin, 240. The difference, 34, is not very different from 2 × H_2O, therefore there is, perhaps, a small portion of 1,4-DHAQ · $2H_2O$ in the samples.

The melting point of the quinizarin is given in Table I. It can be seen that it is the quinizarin obtained from the thin films which gives the best results. It is well known that the melting point varies with the purity of the organic compounds. Therefore, we see in Table I that the product obtained in the thin film form is the purest one. These results exclude any dramatic effect of the small proportion of hydrated quinizarin on the properties of the samples.

This result is confirmed by the elemental analyses (Table I). It can be seen that here also the best results are obtained with the thin films. We can conclude that the subli-

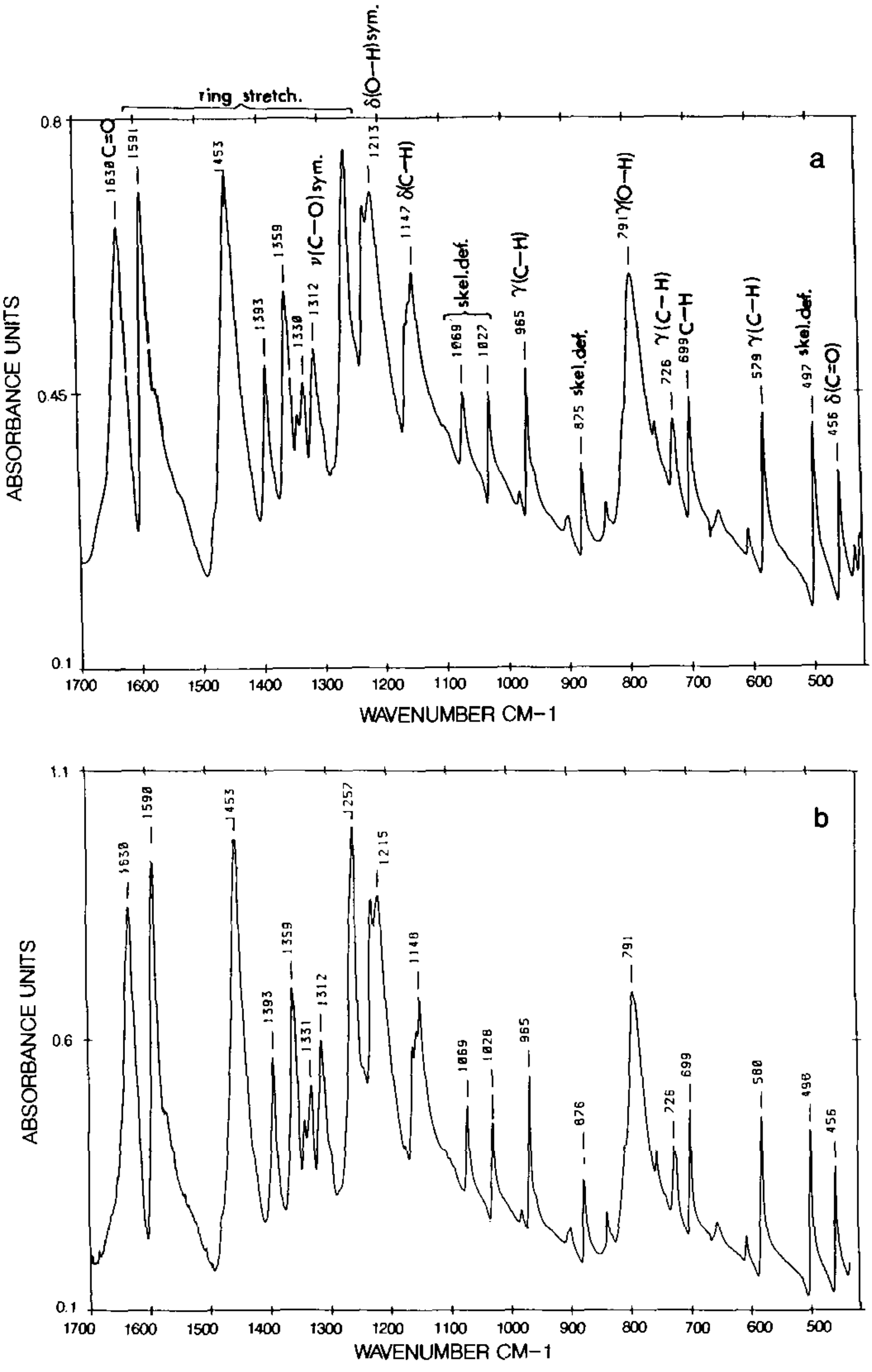


FIG. 1. I.R. spectra for (a) quinizarin powder and (b) quinizarin thin film.

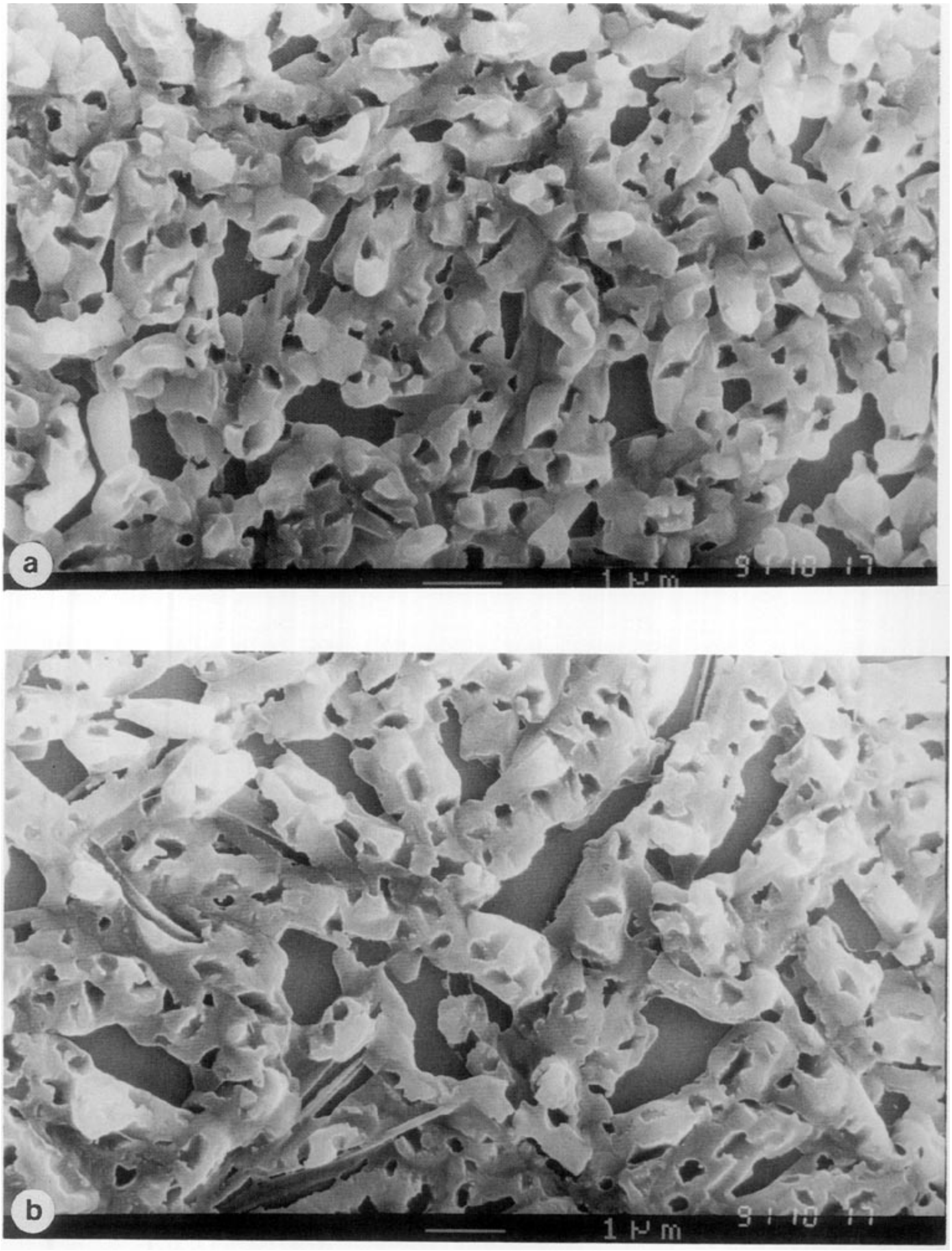


FIG. 2. SEM micrographs showing the variation in morphology with the deposition rate (r) for the quinizarin films. (a) $r = 2$ nm/s, (b) $r = 0.6$–0.7 nm/s, (c) $r = 0.5$ nm/s, and (d) $r = 0.2$–0.3 nm/s.

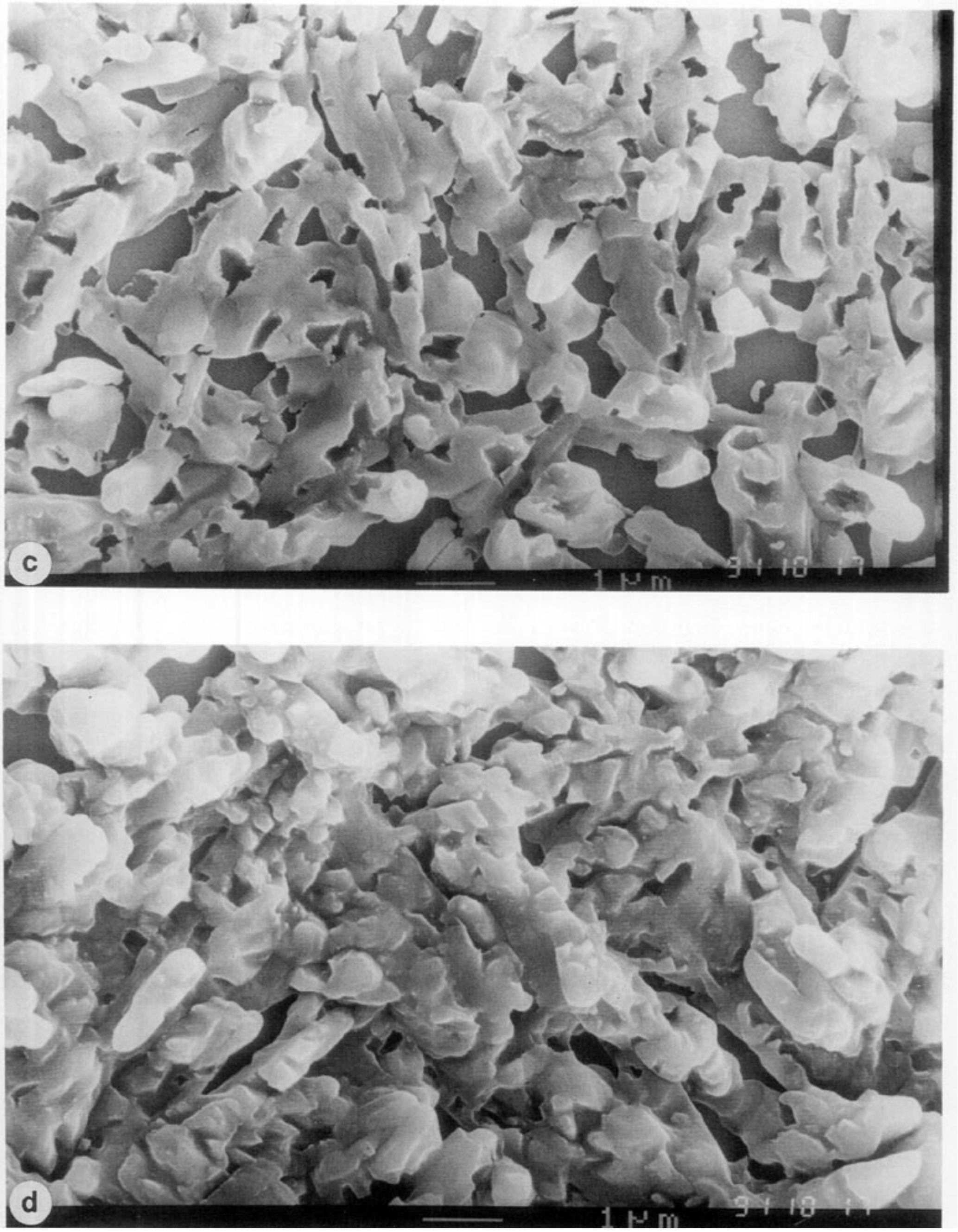


FIG. 2—*Continued*

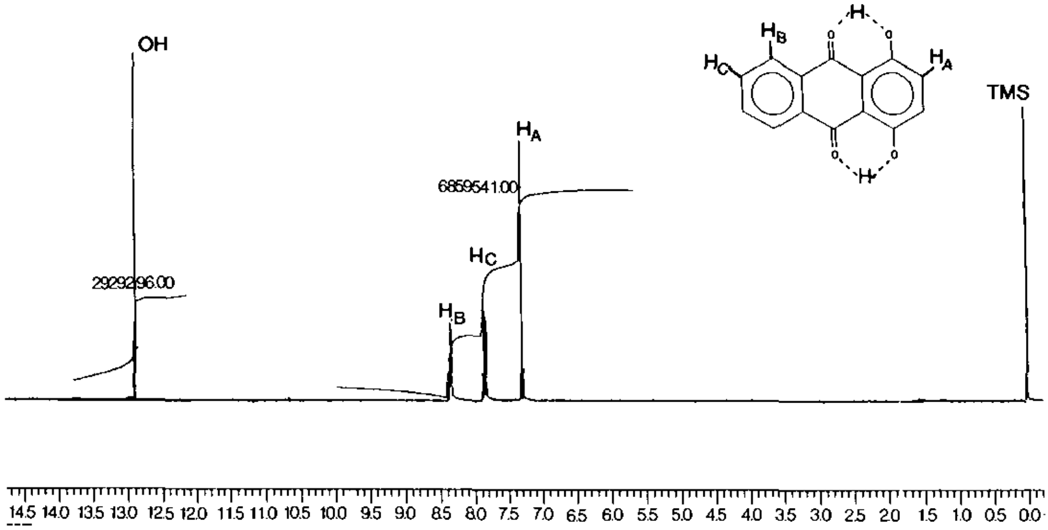


FIG. 3. ^{1}H-NMR spectra for sublimated quinizarin thin film. Inset, basic unit of the molecular structure of quinizarin.

mation under vacuum, in order to obtain the thin film, is also a very efficient process in order to purify the compound. Therefore, we do not need any purification process before the deposition of the films, since the deposition procedure is an efficient purification method, without any decomposition of the product in the temperature range used during the sublimation of the powder.

XPS spectra of the C_{1s} and O_{1s} regions are shown in Fig. 5. The spectra of the powder and of the films are quite similar. We can see that, before etching, there is a small binding energy difference between the peak of the powder and those of the thin films. This energy difference being the same between the C_{1s} peaks or the O_{1s} peaks, we can imagine that this small chemical shift is related to a small charge effect since the quinizarin is an insulating compound. After etching there is a new chemical shift of the peak locations. This small location difference may be due to room air pollution as shown earlier (*9*). Quantitative analysis, before and after etching (Table II), shows that the composition of the powder and of the films are similar. Before etching the difference with theoretical stoichiometric composition may be attributed to carbon and oxygen pollution from the atmosphere as

TABLE I

MELTING POINT AND ELEMENTAL ANALYSES OF DIFFERENT QUINIZARIN SAMPLES

Samples	Melting point (K)	*Elemental analyses* % C	% H
Aldrich powder	464–466	69.5	4.3
Aldrich powder recrystallized in CH_3COOH	469–472	69.3	3.9
Thin film	472–473	70.1	3.8
Theoretical value (*21*)	473	70	3.36

TABLE II

XPS QUANTITATIVE ANALYSIS

Samples	Etching time (min)	at.% C	at.% O
Powder	0	82	18
Powder	3	92	8
Thin film	0	82	18
Thin film	3	92	8
Theoretical value	—	78	22

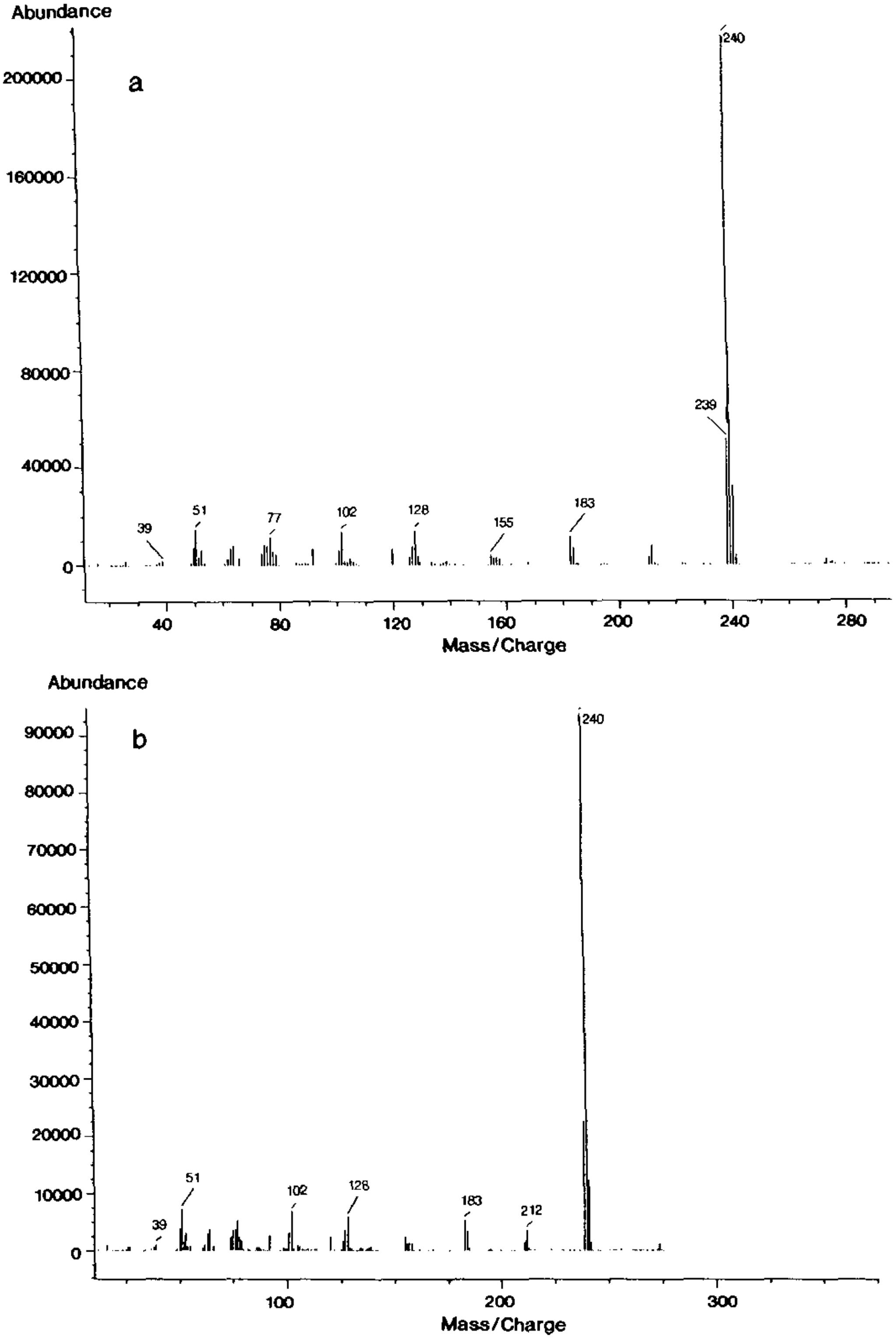


FIG. 4. Positive ion mass spectra (a) of quinizarin powder, and (b) of quinizarin thin film.

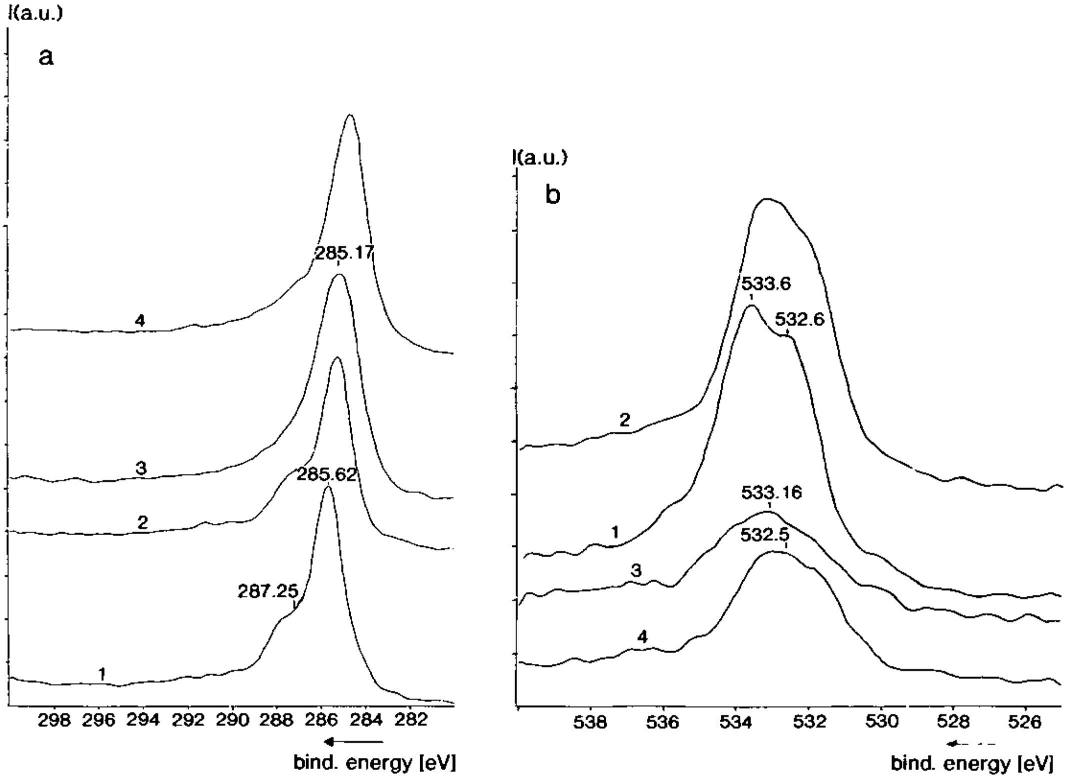


FIG. 5. XPS spectra of quinizarin samples (a) C_{1s}, (b) O_{1s}; before etching (1) powder, (2) thin film; and after an etching of 4 min (3) powder, and (4) thin film.

outlined before. After etching, the etching speed of the carbon and of the oxygen may be different, as discussed below, which may explain the difference between theoretical and measured values. It can be seen in Fig. 5 that the C_{1s} spectrum, before etching, exhibits a shoulder toward the high binding energy. After etching while the shoulder has disappeared the spectrum is skewed towards the high energy side. Therefore, the peak has to be decomposed in order to investigate the different carbon bands.

In the case of the O_{1s} spectrum, the peak is very large and exhibits a strong anisotropy with a shoulder which may be attributed to, at least, two O_{1s} peak superimposed with different binding energies. Therefore, these peaks have to be decomposed. The decomposition of these peaks into different components and the quantitative interpretation, was made after substraction of the background using the Shirley (*22*) method. The developed curve fitting programs permit the variation of parameters such as the Gaussian–Lorentzian ratio, the full width at half maximum (FWHM), the position, and the intensity of the contribution. Examples of the results of these fits are shown in Fig. 6 and 7.

The O_{1s} peak is decomposed into two different components (Fig. 6). By comparison with data references (*23*, *24*) the peak with the smaller binding energy may be attributed to the carbonyl group while the other may be attributed to the hydroxyl group. Systematically, whatever the sample, a quantitative estimation of the composition in atomic percentage gives about 55% of carbonyl group and 45% of hydroxyl group. This discrepancy with the theoretical value may be attributed to some surface pollution with oxidized carbon. In addition, after etching, the

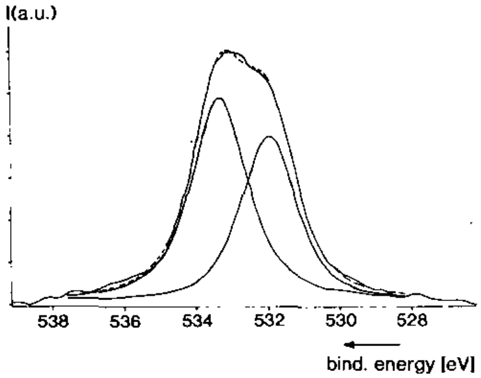


FIG. 6. Result of the O_{1s} curve fitting thin film before etching, (—) experimental curve; (---) fitted curve; and (—) different components.

relative quantity of oxygen decreases, which shows that the etching speed of oxygen is higher than that of carbon. This fact may correspond to some decomposition of the DHAQ during the etching.

Before etching, the C_{1s} peak can be decomposed into three peaks (Fig. 7). The relative intensities of the peaks show that if the first main peak is attributed to the carbon bond in the aromatic cycle then the two others peaks cannot be attributed to the carbonyl and hydroxyl groups since the peak situated at 287.3 eV is far taller than that situated at 290.7. This last low intensity peak can be attributed to the shake-up satellite arising from the aromatic ring ($\pi \rightarrow \pi^*$) (*25*). The amount of carbon corresponding to the peak situated at 287.3 eV (#29 at.%) is of the same order as that which corresponds, theoretically, to the carbon bond in the carbonyl group plus the carbon associated with the hydroxyl group. Any attempts of decomposition of this peak into two components (one for the carbonyl and the other for the hydroxyl) have failed. This result suggests that the hydrogen bond between the carbonyl and hydroxyl structures (*12*, *14*) modify the electron repartition around the carbon engaged in these bonds in such a way that it becomes very difficult to resolve these two peaks. The binding energy of the peak corresponds to a medium value comprised of the C=O and C–O binding energies (*26*).

The optical density is shown in Fig. 8. We have studied the optical density of the film deposited on glass. We have also reported the optical density spectrum of the quinizarin powder dissolved in alcohol. We can see that the shape of the two spectra is identical. The first absorption band is located at around 480 nm and may be attributed to the allowed transition $\pi \rightarrow \pi^*$ arising from the aromatic ring. The low energy value of this absorption band is tied to the red shift effect of the hydrogen bond between the carbonyl and the hydroxyl groups.

It can be seen in Fig. 9 that the same optical absorption spectra is obtained with the Ag/DHAQ structures before annealing. After an annealing (t = 24 hr, T = 375 K) the absorption band (around 480 nm) has disappeared, which may be very interesting in our view to obtain on optical storage medium. We have shown that the low energy value of the absorption band located at 480 nm may be attributed to the red shift effect of the hydrogen bond between the carbonyl and the hydroxyl groups, the corresponding $\pi \rightarrow \pi^*$ transition in anthraquinone being situated at around 350 nm. Therefore we can imagine that after annealing the complex formation between Ag and DHAQ has de-

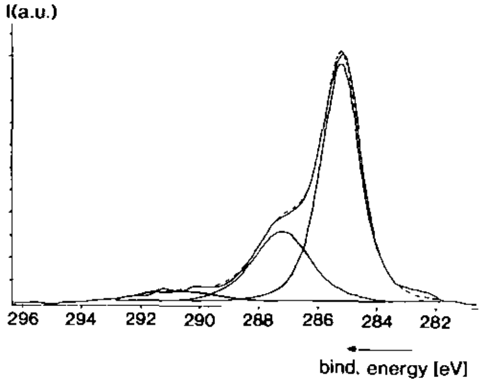


FIG. 7. Result of the C_{1s} curve fitting thin film before etching, (—) experimental curve; (---) fitted curve; and (—) different components.

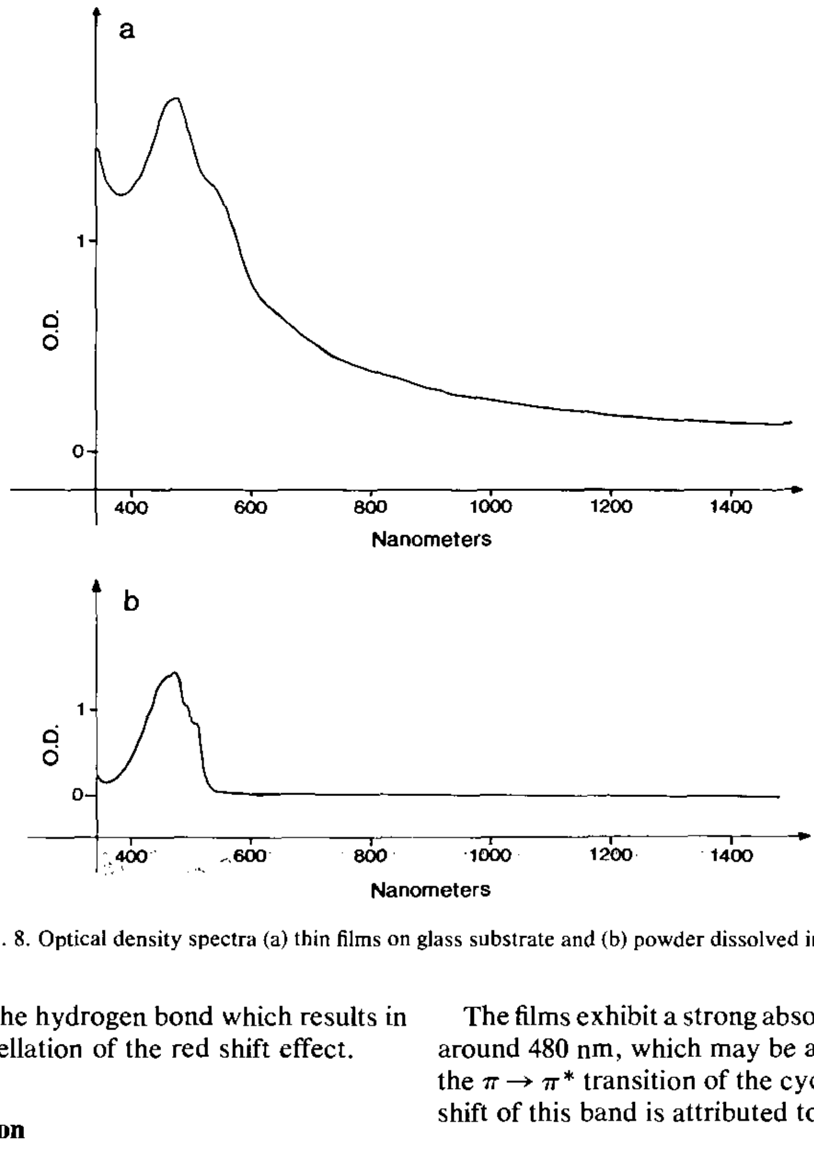


FIG. 8. Optical density spectra (a) thin films on glass substrate and (b) powder dissolved in alcohol.

stroyed the hydrogen bond which results in the cancellation of the red shift effect.

Conclusion

It has been shown that pure quinizarin may be obtained in thin film form by sublimating quinizarin powder under vacuum. When the temperature of the tantalum boat source is monitored to be about 418 K homogeneous films may be obtained without any decomposition of the quinizarin during the process of depositing. Furthermore, the purity of the film is greatly increased by the process. XPS analysis shows the influence of the hydrogen bond, between the carbonyl and the hydroxyl groups, on the binding energies of the constituent elements.

The films exhibit a strong absorption band around 480 nm, which may be attributed to the $\pi \rightarrow \pi^*$ transition of the cycle. The red shift of this band is attributed to the hydro-

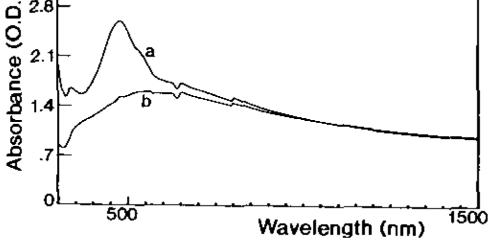


FIG. 9. Optical density of a Ag/DHAQ structure (a) before an annealing and (b) after an annealing (T = 375 K; t = 24 hr).

gen bond between the carbonyl and the hydroxyl groups of the quinizarin. The photochemical hole burning leads to a modification of this absorption band over a very short wavelength domain but at a very low temperature; we have put in evidence a process which permits the modification of the absorption band over a larger wavelength domain but at higher temperatures than in the case of the photochemical hole burning. The first promising results with silver–DHAQ complexes have been obtained. Further work on this study is in progress.

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