A study of the fluorescent properties of spin-coated sodium salicylate thin films

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Abstract

Thin films of sodium salicylate were deposited by spin coating from a solution prepared by dissolving sodium salicylate in methanol. The films were characterized by X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, UV–visible spectroscopy and spectrofluorometry. The films were crystalline with a strong blue fluorescence peak at an emission wavelength of 419.3 nm. The influence of solution concentration, spin speed and annealing temperature on the fluorescence intensity was studied. Optimum results were obtained with a solution whose concentration was 2.5 M. It was found that lower spin speed resulted in higher fluorescence intensity. Moreover, the fluorescence intensity decreased as the annealing temperature was increased. The durability of the films over a period of 30 days was also investigated, and films annealed at higher temperatures were found to be less degraded with time. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Traditionally, research in the vacuum ultraviolet (VUV) region of the electromagnetic spectrum has been dominated by nuclear physics, astrophysics and plasma physics. Recently, however, there has been a growing interest in this region due to the increasing use of synchrotron radiation as a versatile research tool, and the trend to produce sub-micron features using VUV lithography. Such trends have revived the interest in improving conventional VUV sources, detectors and optics, as well as finding new materials for application in this region.

Most detectors (such as photomultiplier tubes) do not detect VUV radiation because their window materials absorb VUV radiation. Thus, fluorescent materials have been used in VUV detection.
Incident VUV radiation is converted into visible light when absorbed by these fluorescent materials (frequency down-conversion). Subsequently, this visible light can be detected by most of the available photomultiplier tubes.

Sodium salicylate (NaC₇H₅O₃) has been the most widely used fluorescent material for VUV detection (30–350 nm). There are a number of features of sodium salicylate (SS) that have contributed to this widespread use [1–3]: its fluorescence intensity (peaked at a wavelength of 420 nm) is matched with the spectral response of most commercial photomultiplier tubes, (2) good sensitivity, (3) short decay time (fast response), (4) high quantum efficiency, (5) linear response over a wide spectral region, and (6) ease of preparation. However, there is a lack of information (or widely scattered values) on some of the basic physical properties of SS such as density, melting point and crystal structure. Husk et al. [4] reported that spray-deposited SS films started to decompose at 100–150 °C, whereas many material safety data sheets (MSDS) [5] reported a value of 200 or 300 °C for the melting point of SS. Moreover, there is considerable variation in the reported values of the quantum efficiency of SS regarding its value and constancy over the excitation wavelength [3]. The spread in the results is caused by aging [4,6], samples of different thickness [3], and different experimental detection and preparation techniques [3]. Possible reasons for aging include: contamination by ambient atmosphere, VUV radiation, absorption of residual gases and water vapor [2]. A value of 65% for absolute quantum efficiency for excitation radiation between 40 and 340 nm seems to be a suitable compromise [3], although SS should be used with caution below 180 nm as its quantum efficiency in this region depends on the energy and flux of the VUV radiation [4].

SS layers have been mainly prepared by spray- ing a saturated solution (e.g. 0.5 M) [7] of SS in methanol onto a glass substrate. The duration of spray controls the thickness of the deposited layer. This results in a fine crystalline layer of SS [3] that is far from being compact and full of voids [7]. Other deposition techniques have been rarely used for preparing SS layers. These include evaporation from a liquid source [8], and sol–gel deposition [9].

The purpose of this work was to prepare SS thin films using a spin coating method, which is a fast, simple, reproducible and low-temperature deposition technique. The effects of the spin speed and annealing temperature on the physical properties of the films were investigated. An attempt to correlate these properties with the fluorescence of SS was made.

2. Experimental

The spin coating solution was prepared at different concentrations ranging from 0.5 to 4 M by dissolving controlled amounts of SS powder (99%) into methanol (99.9%). For each concentration, the solution was stirred for 20 h and then filtered (5 µm) prior to deposition. The SS films were deposited onto BK7 glass substrates using a spin coater (Laurell WS-400A). The solution was deposited with spin speeds (ω) of 2000, 3000 and 4000 rpm for 30 s. The fluorescence spectra were measured at room temperature, in the reflection mode (front surface geometry at an angle of incidence of 45°), using a fluorescence spectrophotometer (SLM AMINCO SPF-500), equipped with a 150-W Xe lamp. The excitation wavelength was 250 nm. It was found that the fluorescence intensity of the films prepared from these solutions increased with the solution concentration. However, for concentrations higher than 2.5 M, the films were visually non-uniform. Therefore, in this work, only the solution with a concentration of 2.5 M was considered. For each speed, three samples were deposited. The samples were annealed at temperatures of 100, 200 and 300 °C, all in air and for 1 h. Annealing was necessary to remove any excess solvent. Annealing at 300 °C resulted in a substantial reduction in the fluorescence intensity since the melting point of SS is between 150 and 300 °C. Therefore, only samples annealed at 100 and 200 °C were considered in this work. The structure of the films was checked by X-ray diffraction (XRD) using a JEOL JDX-3530 X-ray diffractometer, employing Cu Kα (1.54 Å) radiation. The chemical composition of the films was studied using X-ray photoelectron spectroscopy (XPS), and was performed in a VG Scientific
ESCALAB MKII spectrometer using Al Kα (1486.6 eV) radiation. Samples were maintained at ambient temperature at a pressure of 5 × 10⁻⁹ mbar. SS films deposited on tantalum substrates were used for the XPS analysis, so that charging of non-conducting samples could be reduced. The surface topography of the films was checked using a JEOL 5900 scanning electron microscope (SEM). UV–VIS transmittance was measured using a JASCO V-570 spectrophotometer.

3. Results and analysis

3.1. XPS results

Fig. 1 shows an XPS survey scan of a SS film. The scan shows sharp lines due to the main constituents (Na, C and O). The C 1s spectrum (Fig. 2) was deconvoluted into four components which correspond to different bonding states. The first component, at a binding energy (BE) of 284.5 eV, corresponds to the C–H and the C–C bonds [10,11]. The second component, at a BE of 286.2 eV, corresponds to the C–O–Na and the C–O–H bonds [11]. The third component, at a BE of 288.6 eV, corresponds to the C–C=O bond [12]. The fourth component, at a BE of 289.3 eV, corresponds to the O–C=O bond [11]. In addition, there was a weak structure at a BE of 293 eV and it can be associated to shake up of the aromatic ring from benzene [11]. From the areas of the peaks, the proportion of each of these components was calculated and is given in Table 1. The deterioration of the high BE components for the films annealed at 200 °C indicates thermal degradation (decomposition) of the films [12].

3.2. Topography of the films

Fig. 3 shows typical SEM micrographs of SS films annealed at 100 °C (Fig. 3a) and 200 °C (Fig. 3b). The figure shows the presence of white regions that are agglomerates of SS, which may be attributed to inadequacy of the filtering process. The surfaces of the films consisted of circular grains centered around SS particles at 100 °C (Fig. 3a). As the annealing temperature was

**Table 1**

Proportions of the various components of the C 1s XPS spectrum (Fig. 2)

<table>
<thead>
<tr>
<th>T_a (°C)</th>
<th>(1) C–C and C–H (%)</th>
<th>(2) C–O–Na and C–O–H (%)</th>
<th>(3) C–C=O (%)</th>
<th>(4) O–C=O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>40.0</td>
<td>13.8</td>
<td>5.2</td>
<td>41.0</td>
</tr>
<tr>
<td>200</td>
<td>55.6</td>
<td>21.8</td>
<td>7.2</td>
<td>15.3</td>
</tr>
</tbody>
</table>

These numbers correspond to the numbers assigned to the component peaks of the XPS C 1s spectrum (Fig. 2).
increased to 200°C, the circular grains started to diffuse (Fig. 3b), possibly indicating partial melting of the grain boundaries.

3.3. Transmittance and scattering of the films

The experimental transmittance spectra of the SS films are shown in Fig. 4a. The continuous curves are for films annealed at 100°C and the dashed curves are for films annealed at 200°C. As shown in the figure, the transmittance of the films decreased with spin speed. Moreover, the transmittance spectra of the films annealed at 100 and 200°C were nearly the same. Since the bandgap of SS is known to be 3.6 eV [4], the low transmittance of the films, in the wavelength range shown in Fig. 4, cannot be attributed to fundamental absorption. Rather, it may be attributed to scattering.

Light scattering occurs both at inhomogeneities in the volume and at the surface of the film [13]. Both effects lead to the attenuation of transmittance and enhancement of absorption [13]. In the SS films, inhomogeneities are caused by the rough surfaces of the films. Scattering is largely dependent on the size and shape of the scattering particles. SEM micrographs revealed that the SS particles’ size ranged between 10 and 30 µm, and were almost circular in shape. Such a particle size is larger than the wavelength of light (0.4–0.8 µm) and results in Mie scattering. For this type of scattering, the scattered intensity varies as $I_{sc} \propto \lambda^{-4}$. Therefore, the transmittance ($T$) can be written as

$$T = \alpha - \frac{\beta}{\lambda}.$$  (1)

In Eq. (1), the first term ($\alpha$) is a constant that depends on the reflectance of the film. The second term represents the loss in transmittance due to scattering, where $\beta$ is a constant. This equation was used to fit the experimental transmittance spectra of Fig. 4a. The fit is shown by the open circles in Fig. 4b. The excellent fit shown in Fig. 4b indicates that the transmittance spectra were dominated by scattering in the films.

3.4. Surface density of the films

Due to the large scattering in the films, it was difficult to determine their thickness optically.
using interference maxima and minima. Therefore, a weighing technique was employed to measure the surface density ($\sigma$) of the films, which was taken as a measure of the thickness of the films.

The surface densities of the films (in mg/cm$^2$) were: 0.237 (for 2000 rpm), 0.158 (for 3000 rpm) and 0.118 (for 4000 rpm). After many depositions, it was found that the surface density, for a given $\omega$, was reproducible to within 4%. Using a value of 1.8 g/cm$^3$ for the density of SS [14], it can be seen that the thickness ranged roughly from 1.3 $\mu$m (2000 rpm) to 0.66 $\mu$m (4000 rpm). The surface density was inversely proportional to the spin speed (i.e. $\sigma \propto \omega^{-1}$). Annealing the films at 200 $^\circ$C did not change the surface density of the films, indicating a minimal change in thickness upon annealing. A similar behavior was observed with other spin-coated films [15].

The final thickness of a spin-coated film is controlled by two processes. At the start of spin coating, outflow radial convection, due to centrifugal forces, dominates [16,17]. As time progresses, solvent evaporation takes place, and eventually dominates because of the increased viscosity of the spin solution [16,17]. It was observed that the final film thickness decreases as the spin speed increases. The reason is that, for high $\omega$, the fluid is sheared to a large extent, inducing shear thinning of the material [17]. Previous thickness measurements indicated an $\omega^{-1/2}$ dependence of the final thickness [16–18]. The surface density can be written as $\sigma = \rho d$, where $\rho$ is the volume density and $d$ is the thickness of the film. In our case, $\sigma$ was proportional to $\omega^{-1}$. If $d$ was proportional to $\omega^{-1/2}$, then $\rho$ was proportional to $\omega^{-1/2}$, i.e. the volume density of the films was strongly dependent on the spin speed.

The surface density may be related to the transmittance spectra (Fig. 4) in the following way. Higher surface density implies higher density of scatterers, which subsequently implies higher scattering intensity and a reduction of transmittance with decreasing spin speed. However, if the energy of the incident radiation is higher than the bandgap of SS (VUV radiation), then higher surface density implies higher absorption, and therefore higher fluorescence intensity.

Although lower thickness gave lower fluorescence intensity (Fig. 6), it may be more preferable for VUV experiments, which are usually done in the transmission mode. Indeed, the fluorescent material should be thick enough to absorb all of the incident VUV radiation, while remaining transparent for the generated visible photons [19]. Upon comparing the surface density of the spin-deposited films with that of spray-deposited coatings [3,7], one can see that spray deposition is capable of producing thicker films, even with less concentrated solutions. In spin deposition, thickness can be increased by one of three ways: repeated deposition/calcination cycles [20], lower spin speed, and using a more concentrated solution [16]. The first method is not applicable to SS, as the high calcination temperatures involved are much higher than the melting point of SS. Lowering the spin speed or increasing the
solution concentration resulted in very non-uniform films.

3.5. Structure of the films

A typical XRD pattern of an SS films is shown in Fig. 5. Sharp and intense peaks were observed, indicating a high degree of crystallinity. The peaks positions are in good agreement with those of powder SS (Joint Committee on Powder Diffraction Standards (JCPDS) card 01-0013). These spectra were fitted assuming a monoclinic crystal structure [21] and the best-fit values to the lattice parameters were: \( a = 14.7 \text{Å}, \quad b = 12.8 \text{Å}, \quad c = 8.2 \text{Å} \) and \( \beta = 94.3^\circ \). The peaks assignments shown in Fig. 5 are based on these values. The crystallite size was estimated from the Scherrer formula [22]:

\[
L = \frac{0.9 \lambda}{B \cos \theta}
\]

where \( L \) is the crystallite size, \( \lambda \) is the Cu K\(_\alpha\) wavelength, \( B \) is the full-width at half-maximum of the XRD peak, and \( \theta \) is the corresponding diffraction angle. The crystallite size calculated from this formula is shown in the inset of Fig. 5. It is observed that the crystallite size first increases with \( \omega \) and then decreases. The dependence of crystallite size on \( \omega \) is not clearly determined. Some previous studies showed that the crystallite size increases with \( \omega \) [23] while others indicated an opposite behavior [18]. Moreover, there was a reduction of crystallite size for the higher annealing temperature (200 °C). A possible reason for this effect is that an annealing temperature of 200 °C is possibly close to the melting point of SS. Therefore, the molecules would start to mobilize and collisions between them would increase, resulting in a reduction in crystallinity. Such a reduction in crystallinity due to collisions was observed for Gd\(_2\)O\(_3\) films [24]. This may be further supported by the coalescence of the grain boundaries shown for the higher annealing temperature (Fig. 3b). Finally, the thermal decomposition of the films at the higher annealing temperature would certainly reduce the crystallinity of the films due to the change in the chemical bonding of the molecules.

3.6. Fluorescence of the films

The fluorescence spectra of the SS films are shown in Fig. 6a for various spin speeds. The spectra show a broadband extending from 370 to 550 nm peaking at \( \lambda_P = 419.3 \text{nm} \), with a full-width at half-maximum of 63.9 nm. This value of \( \lambda_P \) for the SS films is very close to that of pure SS powder (\( \lambda_P = 421.8 \text{nm} \)).

The dependence of the fluorescence intensity on the spin speed and annealing temperature is shown in Fig. 6b. Since the fluorescence measurements were carried out in the front surface geometry, it is expected that the fluorescence intensity increases with the concentration of the fluorescent material because the effects of re-absorption will be minimal. Moreover, it was shown (Section 3.4) that the concentration (or surface density) decreased with the spin speed. Thus, the fluorescence intensity decreased with increasing spin speed as shown in Fig. 6b. A similar behavior was observed for spray-deposited SS coatings, where the peak fluorescence intensity increased with surface density for values less than 1 mg/cm\(^2\) [3].

Annealing at a higher temperature (200 °C) resulted in a reduction of fluorescence intensity. The effect of annealing on fluorescence intensity can be ascribed to the thermal decomposition of the films at the higher annealing temperature (Section 3.1). A similar reduction in the fluorescent intensity upon annealing was observed in

![Fig. 5. A typical XRD spectrum of an SS film. The inset shows the variation of crystallite size with spin speed and annealing temperature.](imageurl)
3.7. Durability of the films

The durability of the SS films is an important factor, especially for VUV experiments, which usually involve long durations. To this end, the fluorescence intensity of the SS films was continually monitored over a period of 30 days. Throughout that period, the samples were kept at ambient atmosphere and all measurements were done in air. It was found that for the films annealed at 100 °C, there was a reduction of fluorescence intensity with time. At the end of the period, the reduction was 12% (2000 rpm), 8% (3000 rpm), and 6% (4000 rpm). For films annealed at 200 °C, the reduction in fluorescence intensity was 5% for all types of films. Degradation of fluorescence intensity may be related to the absorption of moisture by the films since SS is known to be hygroscopic [2,3]. This absorption increases with the porosity of the films, which subsequently increases with surface density and decreases with annealing temperature. A similar result was observed by Kumar et al. [2] for spray-deposited films, where the intensity decreased by 16% after keeping the samples for 24 h in an atmosphere with 55% relative humidity. It should be mentioned that in addition to this environmental degradation, there is degradation due to the long exposure to VUV radiation, which is dependent on the energy and flux of the radiation [3,4].

4. Conclusion

In summary, thin films of sodium salicylate were prepared by spin coating. The films were crystalline with a peak emission at 419.3 nm. The fluorescence intensity of the films and their surface density increased as the spin speed decreased. Higher annealing temperature did not affect the surface density, but reduced the crystallinity and the fluorescence intensity of the films. Moreover, thermal decomposition was observed in the films annealed at 200 °C. Surface density was the major factor affecting the fluorescence density. The reduction of fluorescence intensity with annealing temperature may be attributed to the thermal decomposition with the higher annealing
temperature. Films with smaller surface density and annealed at a higher temperature were found to be less degraded with time.

Acknowledgements

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References

[5] See for example, the MSDS of sodium salicylate provided by the Physical & Theoretical Chemistry of Oxford University, which lists a value of 300°C for the melting point of SS. However, the MSDS provided by EMD Chemicals Inc. reports a value of 200°C for the melting point of SS.