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Pulsed-laser deposition of selenium

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The preparation and characterization of amorphous selenium thin films grown by pulsed-laser deposition (PLD) is presented. Two laser excitation regimes at 1064 and 532 nm were studied. Interesting relations between the surface quality and the different experimental parameters were found. High-purity thin films were produced with surface quality similar to that obtained by a thermal process. A study of the emission spectra of the plasma generated during ablation is included.

1. Introduction

Pulsed-laser deposition (PLD), is a thin-film preparation technique. The energy for the evaporation is provided by light in or near the optical frequencies. The power generated by an intense pulsed-laser focused on a target is enough to vaporize almost any material. The vapours then deposit on another surface to form a thin film.

The importance of this technique is increasing due to its advantages over other methods: small targets may be used, the evaporation preserves the stoichiometry of rather complicated mixtures, the method is clean, simple, and thickness can be precisely controlled [1, 2].

A major obstacle encountered in the evaporation of some materials is that very small liquid droplets are expelled together with the desired vapour, and the film may be badly splashed by these relatively large particles. A mechanism which has been suggested as responsible for this effect is the excessive heating of the layer just below the target's surface [3]. This process is related to the optical absorption coefficient, the thermal conductivity and the morphology of the target.

Amorphous selenium has been used extensively in hardcopy devices owing to its optoelectronic properties [4]. There is renewed interest in this material, because non-linear optical effects have been recently reported in thin films grown by thermal deposition [5].

To our knowledge, there is only one study of the PLD process in selenium films [6]. It describes the growth rate as a function of laser power and the thickness variation of the film depending on the angle relative to the target surface. However, little attempt was made to characterize other properties of the films.

In this paper we report the production and characterization of amorphous selenium thin films grown by PLD, as well as a brief study of the emission spectra of the generated plasma.

2. Experimental procedure

2.1. Sample preparation

High-purity selenium granules (99.999%) were crushed and pressed at 15 ton to make tablets 2 mm thick and 13 mm diameter, these were used as targets. The substrates were 1 mm thick, they were obtained from glass microscope slides previously cleaned with alcohol and/or acetone. Target and substrate were placed inside a vacuum chamber with a diffusion pump yielding pressures of 5×10^{-5} torr (1 torr = 133.322 Pa). The target was rotated with an electric motor to avoid depletion of material at any given spot.

2.1.1. Infrared (IR) PLD

In a first series of experiments, the fundamental frequency (1064 nm) of a home-made passively Q switched Nd:YAG laser was used to perform the ablation. The energy per pulse was 300 mJ, its duration was approximately 100 ns and the repetition rate was 5 Hz. The output was focused on the target with a 140 mm focal length lens yielding a power density of 5×10^{8} W cm^{-2}. The general apparatus is shown in Fig. 1.

The target was placed 10 mm behind the focal plane and the substrate was placed within a range of 40–70 mm from the target. 500 laser pulses were shot per sample. The films exhibited a large number of small granules on the surface. In order to reduce this splashing, attempts were made to make the target more homogeneous. To this end, the tablets were heated at 150 °C in a graphite container for 45 min prior to evaporation. The melting temperature for selenium is 240 °C [7].

A constant electric field of 200–300 V between the target and substrate was applied to increase the speed of deposition [8]. The splashing was further reduced by placing the substrate on one side of the vacuum chamber, outside the main plasma flow which is perpendicular to the target's surface.

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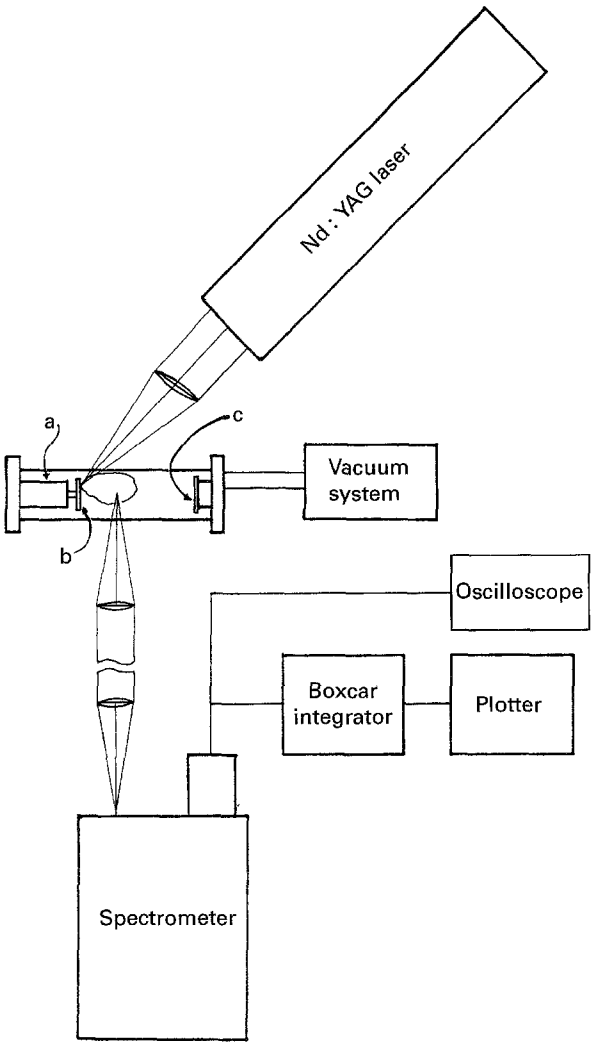

Figure 1 Experimental apparatus; a, motor; b, target; c, substrate.

2.1.2. Visible PLD

In a second series of experiments, we used a frequency-doubled Nd:YAG commercial laser as the ablation source. The maximum energy at 532 nm was 550 mJ, pulse duration of 10 ns and repetition rate of 10 Hz. The number of pulses per sample was varied within the range 2000–3000, with a distance between substrate and target of 28 mm. The splashing effect was greatly reduced.

2.2. Characterization techniques

2.2.1. Optical transmission spectrophotometry

The optical absorption spectra of the films, wavelength versus the absorptance logarithm, were obtained with a Varian UV–NIR spectrophotometer. Wavelength scans ranging from 300–2500 nm were made. Scans going further in the IR or UV were not performed because of the high absorption coefficient of moisture, substrate and/or film.

2.2.2. Surface topography

Scanning electron micrographs were taken for some samples with scales ranging from 10–50 μm. The average size of the droplets and their density were measured directly from the micrographs. To quantify the splashing of the films, a diffuse reflectance method was used in addition to SEM. The spectrophotometer uses an integrating sphere over 97% of the solid angle, whereas the remaining 3% near the specular component is rejected.

2.2.3. Structural and compositional analysis of the films

A conventional X-ray diffraction (XRD) technique was used to analyse the structure of the films. It was checked that the obtained samples were amorphous. The composition of the films was studied with Auger electron spectroscopy (AES). Ion-beam erosion was employed in order to analyse the films at different depths.

2.2.4. Spectroscopy of the laser-generated plasma

The light emitted from the plasma generated by the laser pulse was collected by a 15 cm focal length lens placed at the focal plane. This light was steered by a mirror and fed into a 0.01 nm spectral resolution spectrometer through a second lens focused at the entrance slit. The signal was detected with a photomultiplier and fed into a boxcar integrator. The electronic system was triggered by a reference signal coming from the Pockels cell of the laser, and delayed so that the laser pulse was avoided.

3. Discussion

3.1. Characterization techniques

3.1.1. Optical path and energy gap

The thickness and refractive index of the films were both measured by analysing the absorption spectra with an optical interference method [9]. This method allows the measurement of both values if the films are considered as non-dispersive media along a convenient frequency range. However, when the surfaces are very rough (splashed), the refractive index cannot be calculated via this interference method, owing to the excessive light scattering.

The optical energy gap, E_0, was also obtained from the absorption spectra. The absorption coefficient, $\alpha(\omega)$, for a large number of non-crystalline materials and thin films may be modelled by

$$\alpha(\omega) = A/x = (B/\hbar\omega)(\hbar\omega - E_0)^m \quad (1)$$

where A is the logarithm of the absorptance and x is the film thickness. B is assumed to be a constant in the optical frequency range, and the parameter m normally falls in the range of $1 < m < 3$. Following a recently proposed method [10] it is possible to avoid assuming values for B, m, x and still compute E_0. In this case, A and ω, as well as their derivative $dA/d\omega$, are measured near the absorption edge. The gap and

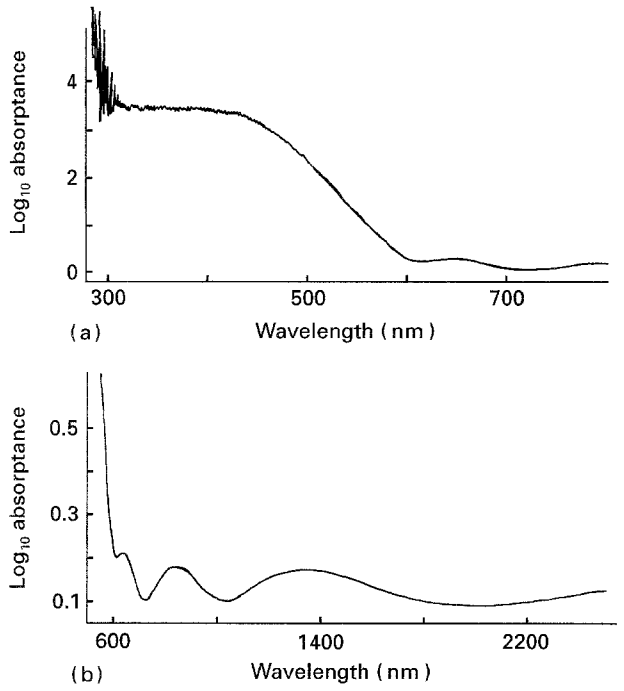

Figure 2 Absorption spectra of amorphous selenium: (a) the absorption edge; (b) the interference fringes.

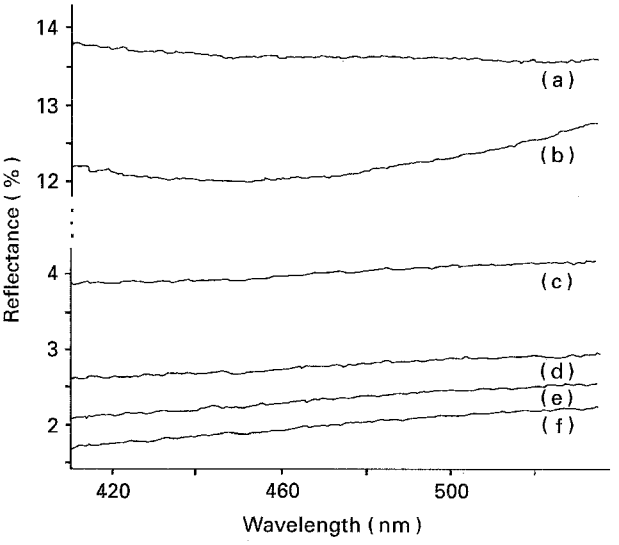

Figure 3 Diffuse reflectance of the selenium thin films versus wavelength for (a) a 0.52 μm thick sample grown under IR excitation, (b) a 0.12 μm thick film grown under IR, (c) a 0.42 μm film grown with full-power green light, (d) a 0.30 μm film grown with dimmer green light, (e) a thermally grown sample, and (f) the diffuse reflectance of plain Mexico City air, for reference.

the parameter m are then obtained from

$$\hbar\omega = E_0 - \left[\frac{\hbar\omega A}{A + \omega(\mathrm{d}A/\mathrm{d}\omega)}\right]m \qquad (2)$$

using the least squares method. The absorption coefficient $\alpha(\omega)$ can be determined from the film thickness and the absorption measurements. In particular, $\alpha(4.74 \times 10^5\ \mathrm{GHz})$ for the He–Ne wavelength at $\lambda = 632$ nm is useful for other non-linear experiments that have been performed on these samples [5]. A typical absorption spectrum is shown in Fig. 2.

3.1.2. Surface topography

While scanning electron micrographs describe with detail the shape of the surface in the picture, they only expose a very small area of the film. The diffuse reflectance method is a simple way to evaluate the average surface roughness, but it does not give more specific information about the light-scattering agents.

3.2. Experimental results

3.2.1. Infrared (IR) PLD

When no electrical field was applied, amorphous selenium films around 0.12 μm thick were obtained. The films exhibited a large number of small granules on the surface. SEM studies revealed splashing droplets with an average size varying from 1–50 μm. The splashing was reduced as the distance between target and substrate was increased. However, the deposition rate was also obviously reduced as this distance increased. When the target was pre-heated, the film surface appeared somewhat smoother. A detailed study of these surfaces has been presented elsewhere [11].

The diffuse reflection measurements shown in Fig. 3b revealed a 12% reflectance for a 0.12 μm thick film.

An electric field was applied to increase the speed of deposition. The underlying mechanism of this process is not yet well understood [8]. We did not anticipate an absolute reduction of the splashing; however, we expected the ratio of splashing over growth rate to be reduced. Indeed, much more material was deposited on the substrate under an electric field, for a given number of pulses. The percentage of diffuse reflectance was around 14%, Fig. 3a, for a much thicker sample than in the previous case (0.52 μm). The splashing was further reduced by placing the substrate on one side of the vacuum chamber, but the deposition rate also decreased.

The optical spectrum of the laser plasma at the target's surface is shown in Fig. 4. The broadband background emission may be fitted to a blackbody radiation of 4278 °C. The peaks which appear superimposed on this curve could not be associated with atomic transitions of selenium nor its ions. The evidence of a thermal process and the large splashing observed on the samples support the heating mechanism suggested as responsible for the evaporation and the resulting surface roughness.

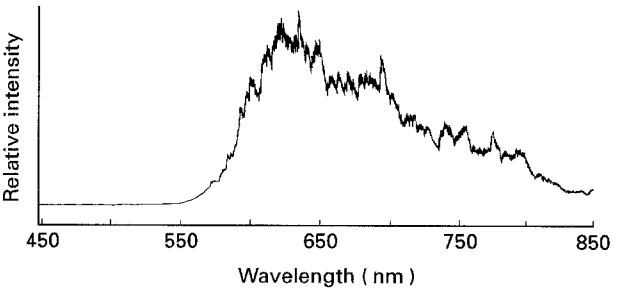

Figure 4 Visible emission spectrum for the selenium plasma generated by IR (1064 nm) excitation.

3.2.2. Visible PLD

At a laser wavelength of 532 nm, the material shows much stronger absorption and the penetration depth is reduced. The layer beneath the surface is not excessively heated as in the infrared case, and the micro-explosions are greatly diminished [12]. The splashing was significantly reduced, as revealed by the diffuse reflectance spectra, which is around 4% in the visible range as shown in Fig. 3c.

An amorphous selenium film of 0.42 μm was obtained after 2000 pulses, with the laser's maximum energy output. The computed refractive index was 2.413 in the 1982–1331 nm range. This result is close to those reported in the literature [7]. The energy gap obtained from the absorption spectrum is 2.07 ± 0.015 eV, which is within the expected values. The energy gap measured in a thermally grown sample, to have a reference, was 2.01 eV.

By decreasing the energy per pulse and increasing the number of pulses to compensate for the lower evaporation rate, the splashing was further reduced. For a film grown with 3000 pulses, at about 70% of the maximum energy output, a 2.75% diffuse reflectance was measured, Fig. 3d. This reflectance is very close to that obtained from a similar thermally grown film as shown in Fig. 3e. Optical interference revealed a refractive index of 2.51 in the 1475–994 nm range and the film was 0.30 μm thick. The energy gap was found to be 2.02 ± 0.024 eV.

AES analysis of the surface revealed the usual impurities at the outermost layer. However, after erosion, the purity of selenium is very high. In particular, the carbon and oxygen impurities are almost non-existent as revealed by the spectrum shown in Fig. 5.

The spectrum of the laser plasma is shown in Fig. 6. Signature peaks of Se^+ and Se^{2+} are clearly observed although non-ionized selenium is absent. There are some other sharp peaks which could not be associated with either selenium or any other residual gases in the cavity such as oxygen or nitrogen. It is likely that these peaks arise from clusters of selenium atoms. On the other hand, there is no clear black body continuous background and thus a thermal process is ruled out as a dominant mechanism. The higher photon energy suggests that a photolic emission prevails. Further studies are under way.

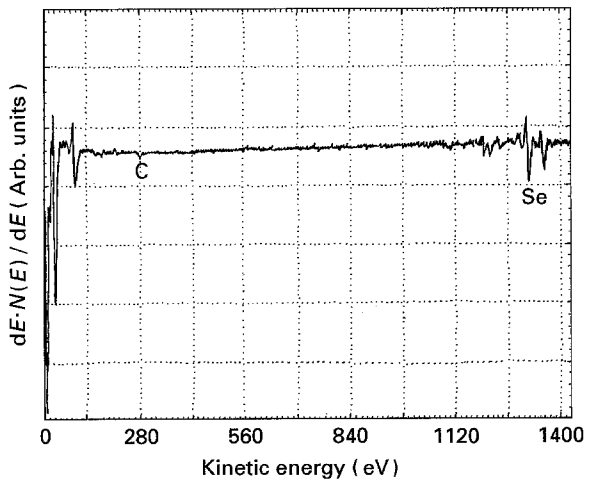

Figure 5 Auger spectrum of a selenium thin film after 10 min erosion.

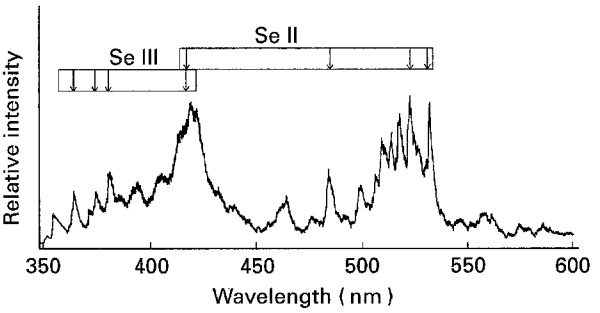

Figure 6 Visible emission spectrum for the selenium plasma generated by green (532 nm) excitation. The Se^+, Se^{2+} transitions with larger oscillator strengths are indicated by arrows.

4. Conclusions

Selenium thin films obtained by PLD show a high density of splashing droplets. This tendency is reduced with a lower energy density per pulse and higher laser frequency, consistent with previous observations [13]. The application of an external electric field increases the rate of deposition. The surface roughness of the optimum samples is similar to that of the thermally evaporated films. They show an amorphous structure with very high purity. The thickness, refractive index and the energy gap of the samples were measured. Diffuse reflectance was used as a quantitative method to measure the average splashing. The plasma's emission spectra are consistent with the compositional analysis of the films, although understanding of the plasma dynamics is still lacking.

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