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Effect of isothermal annealing and visible-light illumination on the AC-impedance behavior of undoped selenium thin films

I.F. Al-Hamarneh [a], B.N. Bulos [b], M.M. Abdul-Gader Jafar [b,*]

[a] *Department of Applied Science, Prince Abdullah Bin Ghazi Faculty of Science and IT, Al-Balqa Applied University, Salt 19117, Jordan*
[b] *Department of Physics, Faculty of Science, University of Jordan, Amman 11942, Jordan*

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ABSTRACT

The effect of post-deposition isothermal annealing (30 °C $\leqslant T_A \leqslant$ 70 °C) and visible-light illumination on the complex AC-impedance of undoped selenium thin films deposited at the substrate temperatures T_S = 30, 50, 70 °C has been studied in the frequency range 0.2–12 kHz. The AC-impedance of amorphous selenium (a-Se) films (T_S, T_A < 50 °C) was mainly capacitive, with no loss peaks being observed in their $Z''(\omega)$–ω curves, irrespective of illumination. This behavior was ascribed to a dominant charge-carrier trapping effect of bulk/surface charged defects usually present in a-Se. On the other hand, the measured $Z''(\omega)$–$Z'(\omega)$ diagrams of illuminated polycrystalline Se samples (50 °C $\leqslant T_S$, $T_A \leqslant$ 70 °C) exhibited almost full semicircles, whereas their $Z''(\omega)$–ω curves revealed prominent loss peaks at well-defined frequencies. As the annealing temperature or light intensity is increased the loci of the points determined by intersections of these semicircles with the Z'-axis at the low-frequency side shift greatly towards the origin, while the loss-peak positions shift to higher frequencies. These experimental findings were explained in terms of a significant increase in electrical conductivity of selenium films due to thermally-induced crystallization at temperatures beyond glass-transformation region of undoped selenium and to creation of electron–hole pairs by visible-light illumination.

1. Introduction

In its solid-state phase, selenium (Se) can coexist in one of its main structural allotropic modifications (e.g., amorphous, crystalline hexagonal and monoclinic structures), which generally composed of different chain-like and/or ring-like molecular microstructures [1–4]. Solid films of amorphous selenium (a-Se) have important applications in digital X-ray medical diagnostic imaging systems [5–7] and in other solid-state devices (like schottky diodes, photovoltaic heterojunctions, and solar-cell devices [8–12]). Undoped a-Se exhibits p-type electrical conduction, possesses very high dark room-temperature DC resistivity (>10^{12} Ω cm) and has an optical band-gap energy $E_g \sim 2$ eV at 300 K [1]. Undoped a-Se usually suffers from thermal instability and aging effects due to phase transformation and structural relaxations even in normal ambient conditions as it has a low glass-transformation temperature, T_g (∼40 °C), which is much higher in the case of slightly doped a-Se material [13–17]. Like other chalcogenides, undoped a-Se is known to contain a high density of bulk/surface traps and localized states due to native (intrinsic) charged defects originating from its lattice disorder and normal broken dangling bonds [1,2,17–20]. This leads to bad electrical performance of devices using a-Se films because of unavoidable electron and/or hole trapping effects [21–23].

Thermal heating of undoped a-Se films at temperatures above 40 °C normally induces prominent structural changes in them [24–26] and transforms them to polycrystalline ones with a hexagonal-like microstructure and a higher electrical conductance [25]. A recent report [27], however, argued that polycrystalline Se films can be deposited at 30 °C and further post-deposition annealing at temperatures far beyond 100 °C did not improve their crystallinity.

The literature is wealthy in papers on DC electrical and optical properties of undoped and doped a-Se films, but not much work has been reported on the AC behavior of undoped Se films subjected to thermal heat treatment at temperatures near and beyond the T_g-region of a-Se [26]. In the present paper, we shall report

* Corresponding author. Tel.: +962 6 5355000-22042; fax: +962 6 5348932.
E-mail address: mmjafar@ju.edu.jo (M.M. Abdul-Gader Jafar).

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further details on the effect of substrate heating and/or post-deposition isothermal annealing at temperatures in the range 30–70 °C on the AC-impedance behavior of vacuum thermally-evaporated thin films of undoped selenium. The effect of visible-light illumination on AC-impedance of these heat-treated selenium films will be also examined.

2. Experimental

Undoped 0.5-µm thick selenium films were deposited onto microscopic soda-lime glass substrates maintained at temperatures T_S = 30, 50, 70 °C using a conventional thermal evaporation method under a base pressure of 10^{-5} Torr. Some of these films were subjected to post-deposition isothermal annealing for 2-h periods at different annealing temperatures (T_A = 30, 50, 60, 70 °C) under dry nitrogen gas atmosphere. It has been noted that these selenium films experienced some re-evaporation and peeling-off when they were deposited and/or isothermally annealed at temperatures near or beyond 80 °C. The structure of the obtained selenium films were determined by a conventional X-ray diffraction (XRD) technique in the $\theta - 2\theta$ scan mode using the Cu Kα radiation of wavelength λ = 0.1548 nm, while the scanning electron microscopy (SEM) was employed to obtain micrographs of their surface morphology.

Pair of 1-mm separated gold (Au) electrodes was deposited on the upper surface of selenium films used in AC-impedance measurements. The samples were shielded inside a vacuum-tight metallic chamber ($\sim 10^{-2}$ Torr) to reduce electrical pick-up/noise, spurious illumination, and environmental contamination (oxidation and/or water adsorption). An AC-impedance apparatus [28] has been employed for measuring room-temperature complex-impedance magnitude, $|Z(j\omega)|$, and phase angle, $\theta(\omega)$, produced by the sample (film plus electrodes) in the frequency range f = 0.2–12 kHz, where $j \equiv \sqrt{-1}$ and ω ($\equiv 2\pi f$) is the AC-signal angular frequency. The uncertainties in the measured values of $|Z(j\omega)|$ and $\theta(\omega)$ were, respectively, ±10% and ±2° at frequencies below $f \sim 500$ Hz and better than ±5% and ±1° over the frequency range 500 Hz to 12 kHz. The experimental values of $|Z(j\omega)|$ and $\theta(\omega)$ were used to calculate the real, $Z'(\omega)$, and imaginary, $Z''(\omega)$, parts of complex AC-impedance, $Z(j\omega) \equiv Z'(\omega) - jZ''(\omega)$, from the relations: $Z'(\omega) = |Z(j\omega)|\cos\theta(\omega)$ and $Z''(\omega) = |Z(j\omega)|\sin\theta(\omega)$.

Visible-light illumination of samples was achieved using an optical set-up [25] that employed a 650-W white-light tungsten halogen lamp combined with a narrow-band visible-light filter and cut-off filters for infrared (heat) and ultraviolet radiations. Three light intensities of I/I_0 = 0.387, 0.512 and 0.693 were selected using neutral density filters, with I_0 being the intensity of light incident on the sample's surface with no density filter being installed in the measuring set-up. The light-intensity readings were stable to better than ±5%.

3. Results

3.1. Heat-treatment effect on the structure and surface morphology of undoped selenium films

Figs. 1 and 2 show the XRD spectra and SEM micrographs obtained at room temperature for some typical undoped selenium films studied in this work. In the 2θ-range studied (10–40°), the XRD patterns of the selenium films fabricated with T_S, T_A < 50 °C show only broad humps with no clear diffraction peaks. These films were red in color and visually semitransparent and their SEM micrographs show smooth and continuous distribution of very fine selenium particles. On the other hand, the XRD patterns of undoped selenium films deposited at T_S = 30 °C and subjected

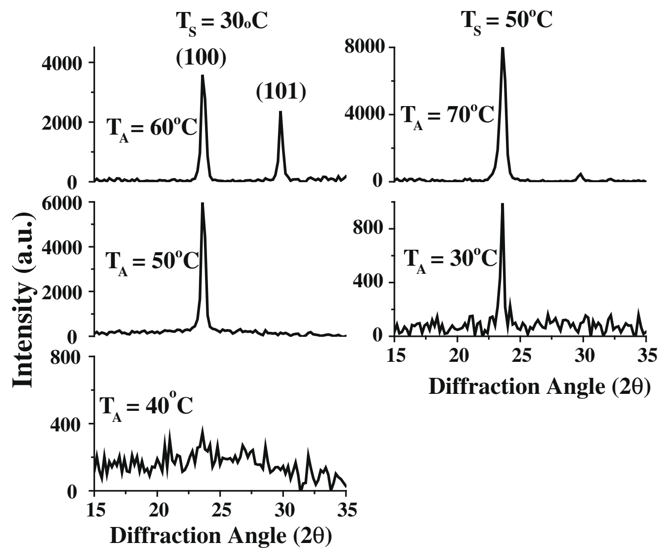

Fig. 1. Typical X-ray diffraction patterns of undoped Se films deposited at T_S = 30 °C and T_S = 50 °C and subjected to post-deposition isothermal annealing at different temperatures.

to post-deposition isothermal annealing at T_A = 50 °C exhibit a prominent reflection peak at the diffraction angle 2θ = 23.8°. At higher annealing temperatures, the XRD diffractogram of these films shows an additional reflection peak at 2θ = 29.8°, the intensity of which seems to compete with that of the former one and tend to become more intense with further increase in T_A. The prominent diffraction peaks obtained for our heat-treated undoped Se films are in good agreement with other XRD diffractograms of Se reported in the literature (e.g., [27,29]). However, for Se films deposited at substrate temperatures near/above 50 °C, only the reflection peak at 23.8° was predominant in their XRD patterns. Our selenium films heat-treated at temperatures T_S, $T_A \geqslant 50$ °C were gray in color with a metallic-like luster surface and more opaque to visible light with their SEM micrographs showing a distribution of irregularly-shaped microcrystalline aggregates of different sizes (0.5–1 µm).

3.2. Effect of heat treatment on the AC-impedance of undoped selenium films in the dark

The behavior of complex AC-impedance, $Z(j\omega)$, of a specimen is often elucidated by plotting its $Z'(\omega)$–ω and $Z''(\omega)$–ω dispersion curves and/or using its linear (or logarithmic) $Z''(\omega)$–$Z'(\omega)$ (complex-impedance) plots [30].

Figs. 3 and 4 show typical linear $Z''(\omega)$–$Z'(\omega)$ plots and semi-log $Z''(\omega)$–ω and $Z'(\omega)$–ω curves taken in dark at room temperature in the range 0.2–12 kHz for undoped selenium films deposited at T_S = 50 °C and subjected to subsequent 2-h isothermal annealing at T_A = 50, 60, 70 °C. We found that the experimental AC-impedance diagrams of our Se films that were fabricated at lower substrate/annealing temperatures had similar behavior when these films were placed in the dark. It is noticed that the dark complex-impedance plots of these heat-treated Se films exhibit only small portions of semicircle-like arcs, which intersect the real (Z'-) axis at the high-frequency side at non-zero $Z'(\omega)$-values. Also, these figures show that the values of $|Z(j\omega)|$ of as-grown and/or heat-treated Se films are so high in the dark ($|Z(j\omega)| > 10^9$ Ω at f < 500 Hz), with $\theta(\omega)$ being near 90°. Fig. 4 illustrates that the dark $Z''(\omega)$ and $Z'(\omega)$ of these films decrease monotonically with increasing frequency, particularly in the low-frequency region,