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CdS thin films formed on flexible plastic substrates by pulsed-laser deposition

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Abstract

The merger of a transparent plastic foil substrate with a semiconductor CdS film for a photonic application was realized using pulsed-laser deposition. Although plastic is not considered to be a favoured substrate material for semiconductor thin-film formation, the deposited CdS film possesses good adhesion, with a polycrystalline texture, flat surface (roughness/thickness = 0.003), and room-temperature photosensitivity with a blue-shifted peak at 2.54 eV. This work demonstrates the capability of pulsed-laser deposition to form novel heterostructures with appealing and useful technological properties such as plasticity and low weight.

(Some figures in this article are in colour only in the electronic version)

The physical and chemical properties of semiconducting thin films are primarily determined during the early stages of growth by the particular deposition technique chosen. Equally important is the choice of the substrate, which critically co-designs the film quality and properties. In the field of II–VI compound semiconductor deposition, Pyrex[®] [1], soda-lime glass [2], quartz [3], and silicon [4, 5] are popular substrate materials because of their availability, cost-effectiveness, and inert character, i.e., they are stable in the required temperature range for common photonic applications, they do not chemically react with the deposited semiconductor, and the hard plane surface makes the formation of optically smooth thin films fairly easy. Pulsed-laser deposition (PLD), specifically of cadmium sulfide (CdS), has attracted notable research activities during the last decade. The films were formed with a continuous wave (CW) laser [6] or pulsed laser beams in the nano- and femtosecond regimes [7, 8], and recently, heteropairing of PLD CdS with cadmium telluride (CdTe) on indium tin oxide (ITO) glass substrates exhibited potential for photovoltaic applications [9]. Emphasizing additional technological applications in optics and optoelectronics, in our previous works, thin-film PLD CdS deposited on glass was used for the realization of green

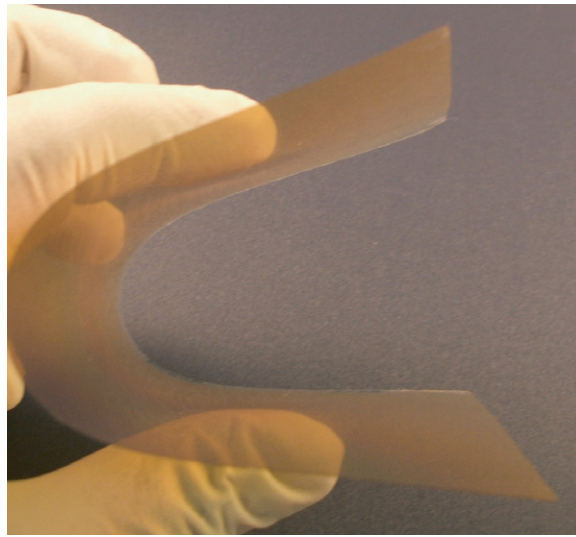


Figure 1. Photograph of thin-film CdS on plastic prepared by PLD.

lasers and the formation of oriented dichroic films [10–13]. In addition, we fabricated a hybrid photovoltaic device based on the merger of PLD CdS on glass with a di-isoquinoline perylene derivative [14]. Despite these promising results and ongoing progress in technology, the inherent weight, rigidity, and fragility of glass substrates excludes glass-based devices from important areas such as aviation, space programmes, and medicine. Therefore, we have explored the possibility of replacing glass substrates with low-weight transparent, unbreakable, and flexible carriers. Our first results are presented in this publication. In fact, by employing PLD, we demonstrate the formation of polycrystalline light-responsive thin-film CdS on a plastic polymer-based overhead transparency commercially available at office supply stores.

The thin-film sample was formed using the PLD setup fully described elsewhere [15]. In order to ablate the material, we employed the pulsed (6 ns, 10 Hz) 532 nm emission of a neodymium:yttrium aluminium garnet (Nd:YAG) laser. The film was deposited in vacuum ($\sim 10^{-4}$ Pa) by exposing the hot-pressed CdS (99.99%) target (Target Materials, OH) to a laser fluence of $2.04 \pm 0.08 \text{ J cm}^{-2}$ for 30 min. In order to optimize coverage of the full standard letter-size substrate with CdS and to avoid the effects of the plume on the plastic, we mounted the transparency on the upper and unheated wall of the vacuum chamber at a distance of 12 cm from the target. The deposited film thickness was approximately 300 nm and the final thin-film–substrate sample is shown in figure 1. However, based on our model calculation for PLD GaAs [16], the film thickness might be not uniform and we presume that a thicker film deposition took place in the region where the longitudinal plume axis was perpendicular to the plastic substrate. In this context, we stress that the plastic substrate did not suffer damage or loss of flexibility due to the plume and, most noteworthy, the CdS film showed good adhesion to the plastic foil and did not peel off when the transparency was squeezed and/or deformed. It must be noted here that no further treatment was performed on the sample after PLD and all results refer to the as-deposited films.

The structure of the CdS film was investigated with standard x-ray diffraction (XRD), and the results are shown in figure 2. The predominance of the (002) peak shows that the *c*-axis orientation of the wurtzite film texture is mainly perpendicular to the substrate. The additional presence of peaks and the fairly broad full width at half maximum (FWHM) of about 1.3°

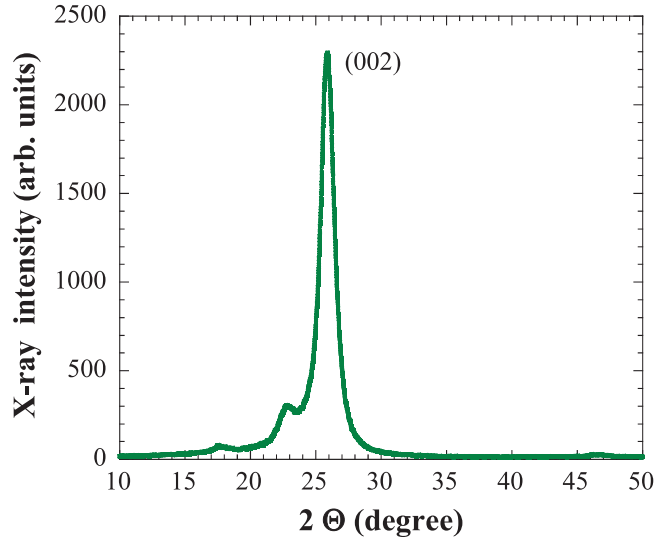


Figure 2. Specular x-ray diffraction scan of thin-film PLD CdS on plastic.

demonstrate that the film is of polycrystalline nature, containing some amorphous parts as well [17]. The results confirm that thin-film PLD CdS does not need a crystalline host in order to arrange itself with ordered texture [18]. This achievement is even more remarkable since the substrate was at room temperature. The average grain size of the film was calculated using the Scherrer formula [19],

$$t = \frac{0.9\lambda}{B \cos \theta_B}, \quad (1)$$

where λ is the x-ray wavelength used ($\text{Cu K}\alpha = 1.54 \times 10^{-10}$ m), B is the full width at half maximum (FWHM) in rad (0.0210 rad taking into account the instrumental broadening, which is 0.0014 rad), and θ_B is the Bragg angle (25.9°). We found $t = 8$ nm, which is 2.7% of the film thickness.

Since our main interest was focused on the investigation of whether these films can be used for photonic applications such as photodetectors, two aluminium contacts with a 1 mm gap between them were evaporated on the CdS surface. The gap between the contacts was excited with low power (typically in the $\mu\text{W cm}^{-2}$ range) monochromatic light, which was provided by the conjunction of a 200 W halogen lamp and a 1/2 m monochromator (Spex 500 M). The photocurrent (PC) was measured and driven with a Keithley 6485 pico-ampere meter and a Keithley 230 power supply, respectively. The PC spectrum was corrected using a calibrated silicon photodiode in order to obtain the responsivity of the sample. The result shown in figure 3 was obtained with an electric field of 100 V cm^{-1} at room temperature. The maximum PC (and therefore the gap energy as well) is shifted towards higher energies beyond 2.5 eV in comparison with previous PC measurements [12], which showed band gap energies of 2.45 eV for films with the c -axis orientation perpendicular to the substrate. It is well known that the band gap energy depends on the particle size, crystal structure, and strain in the film. The band gap increase of nanosized structures is expressed by [20]

$$\Delta E_g = \frac{\hbar^2 \pi^2}{2MR^2}, \quad (2)$$

where, besides the symbols with their usual meaning, M is the effective mass of the system

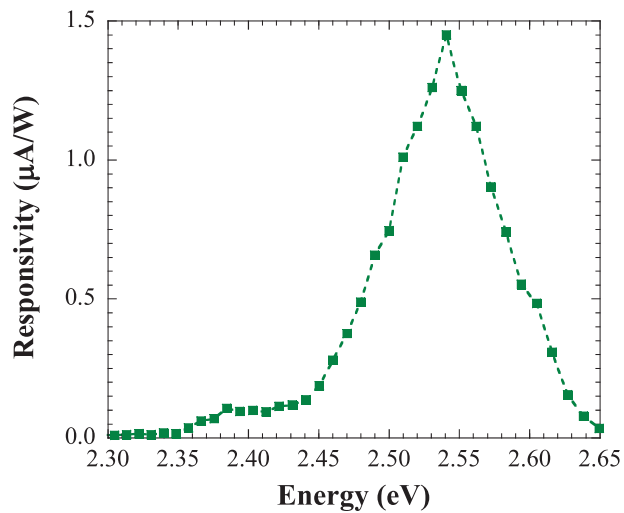


Figure 3. Responsivity spectrum of the thin-film PLD CdS on plastic. The broken line is a guide for the eye.

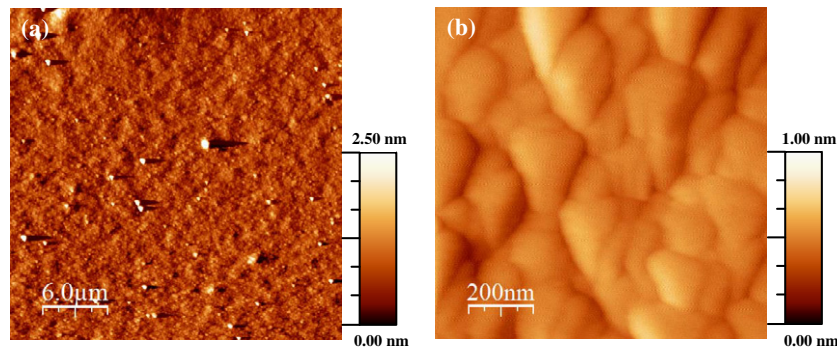


Figure 4. AFM images of thin-film PLD CdS on plastic with (a) micrometre and (b) nanometre resolution.

(1.919×10^{-31} kg for hexagonal CdS) [21] and R is the radius of the crystallites (4 nm according to equation (1)). We find $\Delta E_g = 0.11$ eV, resulting in a band gap of 2.56 eV for the predominately perpendicularly oriented film. The value is in fair agreement with PC maximum at 2.54 eV in figure 3. Thus, it is possible that quantum-size effects are involved in the blue shift. However, increasing strain within the film increases the band gap energy of CdS as well [22]. Since the film thickness is only 300 nm, we think that, in addition to quantum-size effects, strain at the organic–inorganic interface contributes to the blue shift of the PC spectrum. The origin of the blue shift is under current investigation.

The pronounced drop of the PC signal at energies larger than the CdS band gap energy is caused by effective surface recombination indicating a high density of recombination centres at the film surface. However, due to the fair match of the film thickness and the typical light penetration depth of $0.1 \mu\text{m}$ at the CdS band gap, the whole sample can be considered as a surface film without a bulk part.

Atomic force microscopy (AFM) surface images with resolutions in the micrometre and nanometre range are shown in figures 4(a) and (b), respectively. The images were obtained

using Molecular Imaging's PicoSPM II microscope and WSxM scanning probe microscopy program [23]. The images show that the surface is fairly flat with a mean maximum roughness at about 1 nm, resulting in a roughness to thickness ratio of 0.003. Furthermore, the AFM images reveal that the film surface consists of a mosaic structure with large surface features of approximately 100 nm average size. This number exceeds the average grain size calculated from equation (1), but the AFM image does not reflect the crystal size calculation based on x-ray data, since the crystal size found by x-ray analysis is determined by the smallest crystallites through the entire thickness of the film [24]. On the other hand, AFM images may not have the capability to reveal crystalline film substructures, which may cause the discrepancy found. We observed a similar difference in grain size as determined from x-ray data and AFM for low-temperature PLD GaAs on glass as well [25].

In conclusion, we deposited thin-film CdS on plastic employing low-temperature PLD. The samples obtained show good adhesion, have polycrystalline mosaic structure and flat surface, and exhibited useful light sensitivity at room temperature. The results presented confirm the capability of PLD for straightforward inorganic/organic film/substrate merger, which may be used in non-brittle and low-weight optoelectronic circuits.

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