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Surface-relief micropatterning of zinc oxide substrates by micromolding pulsed-laser-deposited films

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ABSTRACT Surface-relief patterning of semiconductor surfaces has become a very active research topic during the last few years. This growing interest is related to the wide range of technological applications of patterned semiconductor surfaces, with particular emphasis on photovoltaic technology. In this work, we show a straightforward, cost-effective and non-hard lithographic approach for transferring surface-relief micropatterns on ZnO surfaces. The method is based on direct micromolding of pulsed-laser deposited ZnO films using surface-modified metallic micromolds. In contrast to those obtained by photolithographic techniques, direct micromolded ZnO surfaces are characterized by very low roughness values on the transferred relief patterns.

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Zinc oxide (ZnO) is a material that has attracted much attention within the materials science community due to its outstanding physical properties (piezoelectricity, electrical conductivity, transparency and light emission capability). These physical properties turned ZnO films into excellent candidates for use in different technological applications such as microelectromechanical systems, sensors, surface acoustic wave elements [1–3] and transparent electrodes [4]. Moreover, ZnO is a well-known II-VI semiconductor compound with a wurzite-type structure and a band gap of 3.37 eV (at room temperature) [5]. As a consequence of its large band-gap and its high excitonic binding energy, ZnO and ZnO-related compounds are promising materials for the development of 300 K short-wavelength lasers [6], as well as for applications in non linear optics [7] and in optical telecommunication systems as a host of Er^{3+} ions for 1.5 μm emission [8].

Periodic surface structures are required in some of these applications. i) As it is well-known, the efficiency of solar cells is improved by light trapping structures that increase the radiation absorption. To achieve this goal randomly textured transparent conductive oxides (TCO), such as ZnO, have been widely employed in polycrystalline-Si photovoltaic technology. So far, light trapping has been achieved through the reflection of light at statistically rough interfaces. The integration of a one-dimensional grating in thin film solar cells leads to a prolonged absorption path in the absorption region compared to structures with flat interfaces, as an alternative to randomly textured substrates [9]. Recently, solar cells with a ZnO periodic grating as a transparent front contact have shown a significant reduction in the overall reflectance [10]. ii) Another outstanding application of surface gratings is the selection of longitudinal modes in distributed feedback lasers. In this application, sub-micrometer gratings are required both for infrared-Er^{3+} and blue-ZnO emissions.

Currently, grating-like ZnO surfaces for solar cell purposes are obtained by photolithographic methods [2, 10, 11]. However, fabrication methods involving hard lithographic techniques are intended to be minimized due to the high costs associated with the implementation of those techniques for large-scale production. Under this focus, there were developed the alternative or unconventional fabrication methods [12–14], which are based on simple, low-cost and straightforward strategies, such as imprinting, molding or stamping. Molding technology has been used for years in the production of diverse surface relief optical components. Conventionally, this technology applies heat and pressure to transfer surface relief microstructures from stamps into plastic substrates. Soft lithography[14] has been used by other authors for patterning metal oxides through micromolding in capillaries of polymeric precursors [15] or by molding ceramic suspensions [16].

The crystalline and morphological characteristics of ZnO films can be selected by using pulsed laser deposition (PLD) technique in a controlled manner [17]. In this work we demonstrate that molding of amorphous oxide films can be obtained by pulsed laser deposition on alkanethiolate-modified metallic stamps. In this case, the alkanethiolate self-assembled monolayer (SAM)

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acts as an efficient anti-sticking molecular coating, promoting an easy release of the deposited film, thus enabling surface-relief transfer with high resolution. This strategy has been previously used to mold metals [18] and hard ceramic materials [19] prepared by thermal evaporation or reactive sputtering. In these cases, the control of temperature (thermal evaporation) and the energy of the arriving particles (reactive sputtering) are key points for the implementation of the molding method as a consequence of the detrimental effects of these variables on SAM stability.

Pulsed laser deposition was performed in a vacuum chamber at room temperature. A KrF laser ($\lambda = 248$ nm, Lambda Physik LPX105i) was used to ablate sintered ZnO (99.99%) ceramic targets rotating at 50 rpm. The laser fluence J on the target was $10\,\mathrm{J\,cm^{-2}}$ and the pulse repetition frequency was 10 Hz. The target-substrate distance was 6 cm. One of the interesting properties of PLD is that the kinetic energy of the species in the laser plasma can be controlled by introducing an inert gas on the deposition chamber. In our case we used Ar as a background gas ($p = 0.05$–0.1 mbar) to thermalize the plasma and thus to promote a "soft landing" of the plasma species onto the micromold surface. The micromolds consisted of sinusoidal grating-like Cu surfaces (pitch, $L = 730 \pm 10$ nm and amplitude, $h = 105 \pm 3$ nm) that were previously modified with a dodecanethiolate self-assembled monolayer (SAM) (Fig. 1 – step 1, Fig. 2a–b). Sample imaging was performed using atomic force microscopy (AFM) operating in tapping-mode. The pitch of the sinusoidal pattern was estimated from power spectral density (PSD) and Fourier analyses (FFT) of AFM images ($50 \times 50\,\mu\mathrm{m}^2$ scan size) – rather than from cross sectional analysis. Fourier analysis gives a more reliable value for the period (pitch) of the sinusoidal profile all over the patterned surface instead of local cross-sectional analysis in a determined region of the patterned substrate. Notwithstanding, in our case, pitch values (L) derived from cross-section analysis are in close agreement with those obtained from PSD and FFT analysis. Surface modification was carried out by immersing a clean Cu micromold during 6–8 h in a 7 mM dodecanethiol solution (in hexane). Then, the micromold was copiously rinsed with pure solvent. By using this procedure it is possible to form a complete self-assembled monolayer on the oxide-free Cu micromold, as deduced from surface analysis by Auger Electron Spectroscopy [20] (AES) (Fig. 2c).

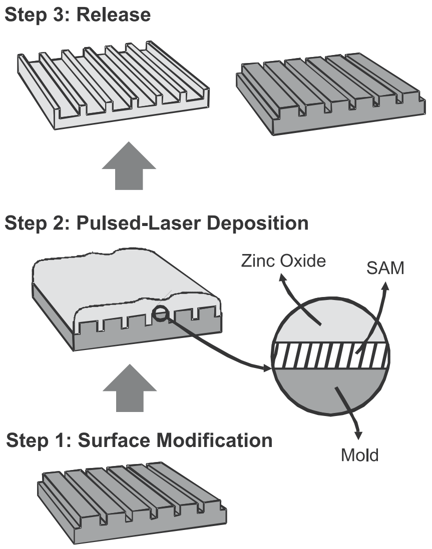

FIGURE 1 Scheme depicting the three different steps involved in the micromolding process. *Step 1:* Surface modification of the micromold by using self-assembled monolayers. *Step 2:* Pulsed-laser deposition onto the surface-modified micromold. *Step 3:* Release of the ZnO pulsed-laser-deposited film from the micromold

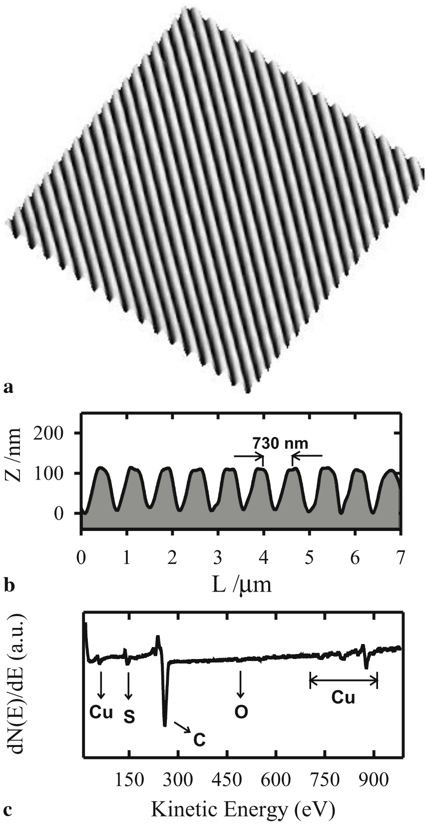

FIGURE 2 (**a**) 3D-AFM image ($13 \times 13\,\mu\mathrm{m}^2$) of the surface-modified copper micromold and (**b**) its corresponding cross-section analysis. (**c**) AES spectrum of the SAM-modified Cu micromold

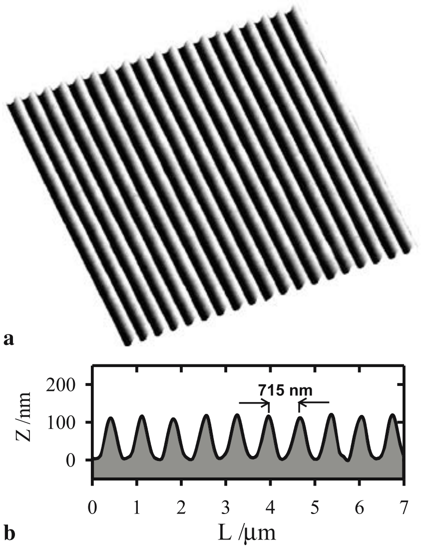

FIGURE 3 (**a**) 3D-AFM image ($13 \times 13\,\mu\mathrm{m}^2$) of the micromolded pulsed-laser deposited ZnO film and (**b**) its corresponding cross-section analysis

Micromolding of ZnO films was performed by depositing a 600–800 nm thick film (deposition time ~ 2 hours) on the SAM-modified Cu micromold (Fig. 1 – step 2) using the experimental conditions described above, that are similar to those employed to obtain amorphous ZnO films. [17] Then, once deposited, the ZnO film is released from the micromold (Fig. 1 – step 3). AFM analysis of the inner surface of the deposited ZnO film clearly shows that a surface-relief grating was micromolded onto it (Fig. 3a). Cross-section analysis of AFM images (Fig. 3b), in agreement with PSD and FFT analyses (not shown for the sake of brevity), demonstrates that the surface-relief grating obtained on ZnO corresponds to a negative-replica of the micromold surface with characteristic dimensions corresponding to $L = 715 \pm 10$ nm and $h = 107 \pm 3$ nm. By comparing the characteristic dimensions of the micromold and those corresponding to the micromolded surface, it can be concluded that no distortion or shrinking effects ($\sim 2\%$) are related to this molding procedure. This fact is a considerable advantage when considering other soft lithographic methods where considerable shrinking effects could be present during post-molding procedures [15, 21] (firing or solvent evaporation). One of the outstanding characteristics of the micromolded ZnO samples is the low density of defects on the patterned relief-structures observed across large scanning areas in different regions of the samples. Another key feature is related to the small grain size ($< 50\,\mathrm{nm}$) of the deposited film achieved by PLD (Fig. 4a–b). These small grains constitute the building blocks of the ZnO relief-structures that were involved in a conformal growth covering the whole micromold surface since the early stages of PLD. Otherwise, some precautions in sample handling must be taken into account during the release step (Fig. 1 – step 3) in order to obtain damage-free patterned ZnO surfaces. Thus, it gives better results to perform the releasing step by using Scotch tape or by gluing the ZnO deposit to a glass substrate.

The methyl-terminated SAM plays a key role as anti-sticking release coating that is required as a consequence of the adherent properties of PLD deposited oxide films on Cu. In other words, the great affinity between the ZnO deposited particles and the Cu surface [22] can be minimized by hydrophobizing the micromold surface with SAMs. In the presence of the methyl terminated SAM, the surface energy of the Cu micromold varies from $\sim 1.9\,\mathrm{J\,m^{-2}}$ [23] to $\sim 29\,\mathrm{mJ\,m^{-2}}$ [24]. This drastic change on the surface energetics is sharply reflected on the diminution of the work of adhesion from $\sim 3.4\,\mathrm{J\,m^{-2}}$ [23] for the system ZnO/Cu to $\sim 44\,\mathrm{mJ\,m^{-2}}$ [25] for the ZnO/SAM/Cu system. The magnitude of the work of adhesion for the system ZnO/SAM/Cu was roughly estimated from adhesion studies on polymer/oxide interfaces reported by Chaudhury and coworkers [25]. Concerning the interaction between PLD plasma species with self-assembled monolayers, this interesting topic has been scarcely studied in the literature. In the presence of background gases, Shigekawa et al. [26] demonstrated that SAMs are compatible with PLD techniques, enduring the interaction with the species generated during the laser ablation process. Site-selective PLD on SAMs has been reported by Hata et al. [27] showing the important role of the terminal group on determining the affinity between the deposited matter and the functionalized substrate. On the other hand, Reinhoudt and co-workers [28] have shown that by means of PLD on SAMs it is possible to build metal–SAM–metal nanostructures. Thus, SAMs serve as a "heat bath" to efficiently dissipate the kinetic energy of the impinging species, as recently suggested by Morris et al. [29]

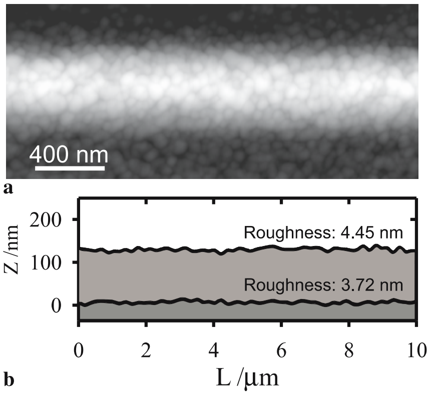

FIGURE 4 (**a**) Top view AFM of the micromolded ZnO substrate showing in detail the granular building blocks forming the surface-relief structure. (**b**) Cross-sectional analysis along (on top and at the bottom) of the micromolded relief structure

Interestingly, we failed when we intended to repeat the same micromolding procedure using gold-made micromolds instead of copper micromolds. In this case the gold micromolds release step is more difficult, or impossible in some cases, suggesting SAM damage. This interesting fact could be explained considering recent results reported in the literature related to sputtering of self-assembled monolayers. Chenakin et al. [30, 31] observed that the stability of alkanethiolate SAM is extremely sensitive to nature of the metal substrate when bombarded with charged species. The character of the degradation kinetics is largely influenced by the binding characteristics of the thiol group (–SH) to the metal substrate. In our case, a stronger affinity of sulfur to Cu than to Au, as derived from thermal-desorption spectroscopy results [32] and ab-initio [33] calculations, enables the SAM to overcome any significant collision-induced degradation during the deposition process.

In conclusion, we have shown a simple, straightforward and low-cost strategy for micropatterning of ZnO by micromolding pulsed-laser-deposited films. The procedure is based on transferring surface-relief micropatterns from an alkanethiolate-modified metallic micromold to a ZnO film pulsed-laser-deposited onto it. The nature of the metallic micromold must be taken into account to avoid the degradation of the anti-sticking coating during the deposition process. The micromolding approach that uses deposition by laser ablation, instead of using slurries or polymeric precursors, clearly shows no significant shrinking effects. This procedure does not involve the repetitive use of hard-lithographic techniques or micromachining processes to transfer surface-relief micropatterns onto the ZnO surface. This is a remarkable advantage if we consider that ZnO films are sensitive to temperature, acids and water, and therefore, they can be damaged during micromachining processes, photolithographic steps or etching procedures. Therefore, PLD on SAM-covered metallic stamps has demonstrated to be a promising route for transferring surface-relief micropatterns to oxide films.

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