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Full Length Article

Study of sputtered ZnO modified by Direct Laser Interference Patterning: Structural characterization and temperature simulation

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ABSTRACT

ZnO thin film sputtered on alumina substrate is processed by Direct Laser Interference Patterning (DLIP). The heat transfer equation has been simulated for interference patterns with a period of 730 nm and two different fluences (85 mJ/cm^2 and 165 mJ/cm^2). A thermal threshold of 900 K, where crystal modification occurs has been calculated, indicating a lateral and depth processing around 173 nm and 140 nm, respectively. The experimentally reproduced samples have been analyzed from the structural and composition point of view and compared to conventional thermal treatments at three different temperatures (600 °C, 700 °C and 800 °C). Promising properties have been observed for the laser treated samples, such as low influence on the thin film/substrate interface, an improvement of the crystallographic structure, as well as a decrease of the oxygen content from O/Zn = 2.10 to 1.38 for the highest fluence, getting closer to the stoichiometry. The DLIP characteristics could be suitable for the replacement of annealing process in the case of substrates that cannot achieve high temperatures as most of flexible substrates.

1. Introduction

Nanostructured and nano-patterned semiconductor surfaces are of great importance in nanotechnology since they can modify material characteristics such as wettability, adhesion [1], electrical and optical properties [2]. Nanopatterning has also been widely used as a template to grow ordered nanostructures [3] and can be implemented in a large amount of applications, from optoelectronics [4] and solar cells [5] to microsensor devices [6].

Nanostructures can be obtained through different techniques such as photolithography, electron-beam lithography and several types of micromachining, but all of them are slow and especially lithographic techniques require a complex and expensive equipment. By contrast, Direct Laser Interference Patterning (DLIP) is a fast, one step, inexpensive and automatable approach able to generate periodic structures in the submicrometric range without the need of a mask [7].

DLIP is based on the interference pattern generated by the interaction of two or more beams exactly on the sample surface [8]. For the 2-beam setup, a series of maxima and minima of interference are formed creating a sinusoidal intensity behavior. Consequently, the area of the material exposed to intensities higher than its ablation or annealing threshold are modified morphological and structurally getting melted or even removed, while areas exposed to intensities lower than these thresholds remain unaffected. The technique has been already investigated for different applications, e.g. to improve optical characteristics of Transparent Conductive Oxides (TCO) for thin film silicon solar cells [9–12] or to form arrays of magnetic dots [13]. Models to predict possible sample topographies of different materials under DLIP processes have also been studied to optimize light trapping in thin-film silicon solar cells [14]: these investigations would also help to determine other possible applications in advance.

ZnO has been selected as target material to process because it has been well studied since 1935 [15] and it presents attractive features for device fabrication such a good stability and non-toxicity. Moreover, it has a large trajectory in the micro and nanotechnology field, especially as a sensitive layer for gas sensing devices [16] or solar cells [5]. Besides, through laser-induced nanostructures on the semiconductor, electrical properties and interaction between the semiconductor and the substrate can be controlled and tuned for specific purposes.

In this work, a 2-beam DLIP setup is used to generate one-dimensional (line shape) structures on sputtered ZnO deposited on alumina. A simulation of the heat transfer equation of structures

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Nomenclature

$C_p(T)$	heat capacity (J/(m·s))
I	intensity distribution of the laser (J/(m^2 · s))
$I_t(t)$	temporal Gaussian distribution (s^{-1})
K	thermal conductivity (W/(m·K))
P	period of the interference pattern (m)
$Q(x,z,t)$	heat source (J/m^2)
R	reflectivity
T	temperature (K)
T_{th}	thermal annealing threshold temperature (K)
$T_{trans.}$	transmittance
$g(x,z,t)$	heat flux (W/m^2)
k	wave number (m^{-1})
m_x	molar mass (kg/mol)
t	time (s)
t_0	pulse arrival time (s)
x and z	position coordinates (m)

Greek symbols

Λ	duty cycle
β	angle between the interfering beams (°)
$\Phi(x)$	energy intensity distribution (J/m^2)
Φ_0	fluence of each interference beam (J/m^2)
α	absorption coefficient (m^{-1})
λ	wavelength (m)
ρ	density (kg/m^3)
σ	standard deviation (s)
τ_p	Full Width at Half Maximum of the laser pulse (s)

with 730 nm of period and two different fluences is carried out with the purpose of finding out the transient temperature as a function of depth inside the ZnO thin film during the laser exposure. The simulated structures are fabricated and experimentally characterized in order to investigate the laser influence both on the thin film surface and in depth from the structural and composition point of view, which to the best of our knowledge, has never been investigated yet. This is relevant in order to study the interaction of the material at the thin film/substrate interface under the laser effect, what is crucial for devices that use substrates sensitives to low temperatures. ZnO samples thermally annealed at 3 different temperatures (600 °C, 700 °C and 800 °C) are also studied and compared with the samples processed by laser.

2. Experimental

ZnO thin films are prepared by RF sputtering in an Argon atmosphere (ZnO target 99.99% purity) on alumina substrate under $5 \cdot 10^3$ mbar of gas pressure. Subsequently, some ZnO thin films are thermally stabilized in a quartz oven at different temperatures: 600 °C, 700 °C and 800 °C during 4 h in synthetic air in order to see temperature annealing effect (the samples will be named TT600C, TT700C and TT800C, respectively). Other samples are processed by 2-beam DLIP setup with a tripled Q-switched Nd:YAG laser source provided by Thales, the Saga HP model (with a wavelength of 355 nm, a pulse duration of 8 ns, a maximum energy of 600 mJ per pulse and a flat-top energy distribution) to obtain 1D interference patterns on the surface. On the setup (Fig. 1), an optical beam splitter divides the laser source into two different beams, afterwards they are reflected in mirrors and finally addressed towards the sample surface with the same incident angle. The exact configuration is explained in detail somewhere else [17].

The period of the interference structure (P) is defined by the angle between the two laser beams (β) and the wavelength (λ):

$$P = \frac{\lambda}{2\sin\frac{\beta}{2}} \quad (1)$$

In order to achieve lines with a theoretical period of 730 nm, an angle around 28.1 degrees has been setup.

To study the influence of the laser fluence, the samples were processed at 85 mJ/cm^2 and 165 mJ/cm^2 and a single shot was used in all the processes. The samples will be named DLIP85 and DLIP165, respectively.

For morphological characterization, JPK Nanowizard 3 Atomic Force Microscope (AFM) was used. Tapping Mode images were obtained using silicon Tap300-G cantilevers with a resonance frequency around 300 kHz.

The film thickness was precisely determined from the cross section analysis performed by a SEM Quanta 3D FEG from FEI Company.

The crystalline structure of the thin films was characterized by Grazing Incident X-ray Diffraction (GIXRD) at 2°of incident angle

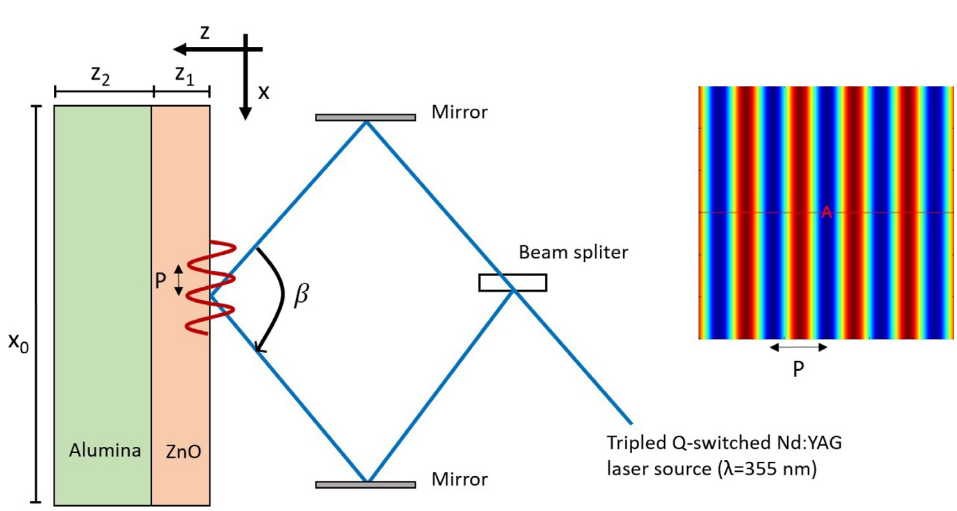

Fig. 1. Schematic two-beam DLIP setup and energy distribution simulation of one dimensional pattern.