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SEM/TEM characterization of periodical novel amorphous/nano-crystalline micro-composites obtained by laser interference structuring: The system HAlO–Al·Al_2O_3

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Abstract

Layers of the metastable, amorphous HAlO are synthesized by chemical vapor deposition from the molecular compound *tert*-butoxyalane ([^{t}Bu–O–AlH_2]$_2$). At temperatures above 500 °C, these layers transform to biphasic Al·Al_2O_3 due to the elimination of di-hydrogen. The interaction of HAlO films with short laser pulses causes partial transformation of amorphous HAlO into nano-crystalline Al·Al_2O_3. Using an interference pattern of two coherent high-power Nd:YAG laser beams produces local and periodic heating, inducing crystallization at equally distant lines in the HAlO layer. Depending on the laser fluence, different morphologies and different amounts of crystalline phases are obtained. In this study, the surface morphology and the distribution of crystalline phases of the structured samples are analyzed using SEM, FIB and TEM. The two-dimensional structures consist of periodic variations of morphology, chemical composition, and phase identity with a well-defined long-range order. When bio-functionalized, the structured samples may be used as carriers for structurally controlled cell-cultivation.

Keywords: Characterization; Nano-crystalline; HAlO film; Nd:YAG laser; Interference; CVD

1. Introduction

Chemical vapor deposition (CVD) is used to produce thin films consisting of aluminum and oxygen from precursors such as aluminum-tris-*sec*-butoxide [1], aluminum-acetyl-acetonate [2], aluminum-hexafluoro-acetylacetate [3] and different alanes [4] including the molecular precursor bis-*tert*-butoxyalane ([^{t}Bu–O–AlH_2]$_2$) [5,6]. At present, controlled deposition of such extended thin films is state-of-the-art. However, for some applications (such as differentiation of cells) the ability of fabricating nanostructures with a well-defined long-range order is highly desired. One method capable of producing such advanced thin film geometries is laser interference structuring [7,8]. This method already has been used successfully to structure such different types of materials as metals [9], semiconductors [10,11], and organic polymers [12]. In this process, coherent laser beams interfere with each other on the sample surface, generating an interference pattern of energy (i.e., line-like or dot-like patterns, depending on the arrangements of the laser beams) with a well-defined lateral long-range order.

The light wave acts as a non-thermal energy source at the sample surface. The electrical field of the electro-magnetic wave interacts with the outer electrons of the material. Depending on the electron configuration and density, the non-thermal energy is absorbed by photo-chemical, photo-thermal, and photo-physical mechanisms [13]. In the case of polymers, photo-chemical bond-breaking and ablation of the material is the main mechanism. In metals the non-thermal energy of the light wave is transformed into heat by electron lattice collisions, the so called photo-thermal process. In semiconductors and ceramics, both photo-physical and photo-chemical processes play an important role. These processes

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result in local melting, re-crystallization, and phase transformation.

Recently we have shown that using CVD on the molecular precursor ($[^tBu–O–AlH_2]_2$) [5,6] produces an HAlO layer consisting of hydrogen, aluminum and oxygen in an equimolar ratio [14]. The reactions during CVD deposition of HAlO are given in the following equation:

$$[(H_3C)_3C{-}O{-}AlH_2]_2 \rightarrow 2H_2 + 2(CH_3)_2C{=}CH_2 + 2/n(HAlO)_n \quad (1)$$

The HAlO layer can be deposited on metallic (e.g., Fe, Cu) or semi-conducting (Si) substrates by directing a gas flow of $[(H_3C)_3C–O–AlH_2]_2$ at reduced pressure on the heated substrate. At surface temperatures above 230 °C, the molecular precursor simultaneously looses hydrogen and *iso*-butene, forming a transparent layer of amorphous HAlO. An $Al{\cdot}Al_2O_3$ $2O_3$ composite is formed from these HAlO layers through heating or CO_2-laser treatments [14].

In a preliminary study, it was shown that it is possible to form micrometer-sized structures of $Al{\cdot}Al_2O_3$ composite on an HAlO layer using laser interference metallurgy [15]. These structures consist of periodic variations of phase identity and topography. With a combination of infrared spectroscopy, X-ray diffraction and electron diffraction, we demonstrated that Al–H bonds are no longer present at the interference maxima. In addition, at these positions, the laser energy gives rise to crystalline γ-Al_2O_3 and metallic aluminum. Thus, the laser treatment not only leads to physical but also to chemical landscapes.

In this study, we extend our previous work [15], placing special emphasis on morphology as a function of laser energy. In addition, the crystallinity of the films after laser treatment is further investigated with transmission electron microscopy (TEM). This enables a qualitative description of the crystallization of the HAlO layer with respect to the local energy distribution during the structuring process.

2. Experimental

2.1. Deposition of HAlO films by CVD

In order to produce a HAlO layer on either Cu or Fe substrates, a copper disc with a diameter of 23 mm and a thickness of 3 mm or a sheet of steel (15 mm × 15 mm, 1.5 mm thick) is placed in a low pressure horizontal cold-wall CVD apparatus as described in Ref. [16]. The substrate is heated for 2 h up to 300 °C by induction and exposed to a constant stream of $[^tBu–O–AlH_2]_2$ at reduced pressure ($\sim 6 \times 10^{-2}$ mbar). The $[^tBu–O–AlH_2]_2$ precursor was synthesized prior to deposition by a reaction between anhydrous $AlCl_3$ and $LiAlH_4$ and a subsequent reaction with *tert*-butanol (^tBuOH), as described elsewhere [5,6]. The precursor reservoir was kept at a constant temperature of 0 °C.

2.2. Laser Interference experiments

A high-power pulsed Nd:YAG laser with a wavelength of 266 or 355 nm, a frequency of 10 Hz and a pulse duration of 10 ns was employed for all laser interference experiments. The beam configuration used in this study to produce a two-beam interference geometry is shown in Fig. 1. Intensity of the individual beams is controlled by choosing suitable lenses and mirrors.

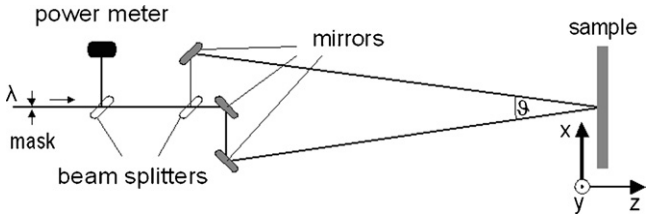

Fig. 1. Scheme of the laser interference system (from [17]).

The structure period can be varied by changing the angle between the individual beams. To obtain a periodicity of 3.3 and 6.3 μm, angles of 6.2° (at λ = 355 nm) and 2.4° (at λ = 266 nm) were used, respectively (λ denotes the wavelength of the laser beam). The laser fluence varied between 230 and 590 mJ/cm^2. Only one laser pulse was used in each individual experiment. Further details of the experimental setup have already been published elsewhere [5,17,18].

2.3. Sample characterization

All samples were imaged with a high-resolution scanning electron microscope (SEM) equipped with a field emission gun (FEI Strata DB 235) at 5 kV acceleration voltage. For TEM investigations, thin foils were prepared with the aid of a Dual Beam Workstation (FEI Strata DB 235) using the electron beam for imaging and Pt deposition and the focused ion beam (Ga^+) for milling of the sample. Initial milling to a foil thickness of 1 μm was performed by employing ion beam currents between 5000 and 300 pA. Using the in situ lift-out method, the thin foil was attached by Pt deposition to a half-grid of Cu. For final thinning, small ion beam apertures of 30 and 50 pA at incident angles between 0.5° and 1.2° were used until the sample thickness was on the order of 70–100 nm. The final step was low kV cleaning at 5 kV.

TEM investigations were carried out with a Jeol JEM 200 CX at an operating voltage of 200 kV. Direct imaging was used to elucidate the microstructure and selected area diffraction, and convergent electron beam diffraction was used to identify phases.

3. Results and discussion

Fig. 2 shows typical structures obtained by two-beam interference patterning (Nd:YAG laser, λ = 266 nm, $\theta = 2.4°$) as a function of laser fluence. In addition, an image of the unmodified surface is displayed. Fig. 2 clearly demonstrates that a well-defined structure develops and that laser fluence strongly influences the morphology of the films.

At laser fluences between 250 and 290 mJ/cm^2 (Fig. 2c), the films remain nearly unchanged at the positions of the laser interference minima. Grooves delimited by a bulge on each side are clearly seen long the lines of the energy maxima. These