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Alpha alumina synthesis by laser treatment of bi-phasic nanowires

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ABSTRACT

Al/Al_2O_3 bi-phasic nanowires (Al-core/Al_2O_3 shell) are prepared by chemical vapor deposition (CVD) using single source precursor (SSP) approach. Such bi-phasic nanostructures were heat-treated using an argon laser operating at visible wavelengths. Al core seems to act as an active binder, which might decrease the inhomogeneous heating and thermal gradients. Nanoindentation method is used to estimate the hardness of the laser treated surfaces. Hardness values and pop-in behaviour in loading-curve indicate a formation of α-Al_2O_3 with very low defect density. It is believed that Al/Al_2O_3 bi-phasic layers exhibit a dynamic change by transforming into alumina after the laser irradiation and this leads to alteration of the optical absorption especially in the visible wavelength region. Following the full transformation to alumina, the surface reflects back the laser light which hinders inhomogeneous and excessive heating. In this context, laser treatment of Al/Al_2O_3 bi-phasic nanowires provides a controlled sintering process which can open up various applications in different fields.

1. Introduction

Alumina (Al_2O_3) is used for broad range of applications where improved heat and thermal shock resistance, wear resistance, oxidation, thermal stability and electrical insulation are needed [1]. In addition alumina acts as a diffusion barrier to mobile ionic species and exhibits high chemical stability [2]. Alumina exists in the form of several polymorphs, such as κ-, γ-, δ-, θ-Al_2O_3 besides the thermodynamically stable α-Al_2O_3 (corundum). Metastable phases, commonly also called "transition alumina" phases [3] can be irreversibly converted to α-Al_2O_3 by appropriate heat treatment. Beside various crystalline alumina phases, α-Al_2O_3 is the hardest and most stable alumina phase with a hardness value of around 28–30 GPa [4].

The degree of crystalinity and the type of existing crystalline phases present in alumina coatings determine final mechanical properties. In protective coating applications α-Al_2O_3 phase is desired in spite of having mixture of different transition phases. In this context a proper heat treatment is needed for the complete phase transformation to α-Al_2O_3 as well as for the densification of the deposited layer [5]. Although all transition alumina phases can be converted to α-Al_2O_3 over 1200 °C, the challenge is to prevent the deformation (by the excessive heating) of the base material which is mostly made of a lower melting temperature metal, metal alloy or even glass-like material. In such cases, the local heat treatment of the deposited layers is desired to obtain dense and pure α-Al_2O_3. In this context, laser is an effective tool for the heat treatment and the sintering of alumina or similar ceramic coatings. In principle, the high energy of the laser beam is used to melt (partially or totally) and to re-solidify the ceramic layers deposited on various substrates [6]. Such laser-assisted heat treatment is an effective way to reduce the porosity and any stresses for obtaining proper microstructure and homogeneity [7].

CO_2 lasers are used extensively for heat treatment and sintering of ceramic coatings since ceramics exhibit high optical absorption at infra-red wavelengths. Although there are various well-established laser assisted ceramic processing methods, it is still a challenge to synthesize fully crystalline, mechanically stable and crack free ceramics by laser treatment. Triantafyllidis et al. showed that, one particular problem of using lasers for surface melting of alumina-based ceramics is the development of thermally induced cracks upon solidification and cooling, resulting from the brittleness of these specific ceramics and the very high thermal gradients and cooling rates that are established due to their high melting temperature and low thermal conductivity [8]. Similar problems are reported by Lee and Zum Gahr, too [9]. Such problems limit the densification level and homogeneity in the phase transformation. In order to enhance the densification by laser treatment, different binders are blended with ceramic particles. Barlow and Vail presented such a binder composition, which is used with high melting inorganic particulates including alumina [10]. The binder helps achieving a dense material at the end. On the other hand,

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such approach is applicable to only powdered materials and after the laser treatment removal of the binder material is needed. Otherwise the residue may lead to the anisotropy in the mechanical and structural properties, which can influence the performance of the material.

Since the optical absorption is one of the key requirements for laser treatment, different binder material formulation has been developed to enhance the optical absorption. There are various methods, which customize the optical absorption by simply blending different ceramic particles. In order to improve optical absorption of alumina particles, Zheng et al. introduced a method comprising coating of them with polystyrene [11]. Coated alumina powders showed better optical absorption and this led to a more homogenous heating and reduced thermal gradient. On the other hand, organic residue stayed as a separate phase after the laser treatment.

In this current work, we proposed a novel method for synthesis of α-Al_2O_3 layers by laser treatment of highly absorbing Al/Al_2O_3 core–shell nanowires. Different than commonly preferred high power CO_2 lasers (output power of several kW), we used a low power Ar laser operating at visible wavelengths since the deposited bi-phasic nanostructures exhibit a high absorption over a broad wavelength spectrum. In addition, due to bi-phasic nature of structures Al core acts as a binder material which enhances densification during the laser treatment. As Al core oxidizes to Al_2O_3 during melting and re-solidification (which reminds of a self-healing material), there is not a trace of a residue at the end as usually observed in case of using an external binder powder for laser sintering of alumina. The dependence of the structural and morphological changes to laser exposure duration (scanning speed) was studied systematically. Mechanical properties of fully dense α-Al_2O_3 layers have been studied by nanoindentation and surprisingly laser treated surfaces exhibit mechanical properties, which are comparable to those of sapphire thin films.

2. Experimental

2.1. Deposition of Al/Al_2O_3 nanowires

Prior to the deposition process, the molecular precursor $(^{t}BuOAlH_2)_2$ was synthesized according to routes given in [12]. Prepared precursor was decomposed on stainless substrates at 600 °C under low pressures (10^{-2}–10^{-3} mbar.) for 30 min. The decomposition was simply carried out by directing a constant stream of the precursor on inductively heated substrates in a CVD cold-wall reactor, which was described elsewhere in detail [13].

2.2. Laser treatment

An air-cooled argon ion laser (Model 2020, Spectra-Physics) operating at multi-line (457.9–514 nm) wavelengths with a maximum output power of 5 W was used to treat deposited layers. The laser beam is kept as a stationary source and the sample was moved relatively to the beam with the help of a XY scanner. The beam was focused by the help of simple plano-convex lens in order to get a fluence of 5.09×10^4 W/cm^2

2.3. Characterization

The coatings were examined using SEM (FEI Quanta 400 FEG) to investigate surface topography of the laser treated zone. As-deposited and laser treated coatings were characterized by an X-ray diffractometer (Siemens, D-5000) using Cu-K$_\alpha$ radiation for elucidation of the crystal structure and phase characterization. Mechanical properties of the laser treated layers were characterized by a Triboindenter® (Hysitron Inc., Minneapolis, MN) Nanomechanical Testing System utilizing a Berkovich tip. Within this system the diamond indenter served as both the indenter probe and an imaging probe. Therefore, it was possible to image and characterize the surface of the layer with the tip and locate the tip on specific position on the surface and perform the nanomechanical testing. The hardness and reduced elastic module were calculated using Oliver Pharr method [14].

3. Results and discussion

SEM image given in Fig. 1a shows that deposited layers are in the forms of tangled and randomly distributed nanowires. The diameters of nanowires stay around 20–25 nm and their lengths are several micrometres. Previously we showed the structure of these bi-phasic nanowires in detail by using transmission electron microscopy (TEM) [15]. These nanowires consist of a metallic aluminium core and amorphous aluminium oxide shell. While fine Al crystallites were observed in the core structure, aluminium oxide shell seems to be non-crystalline. Although we conducted a detailed analysis on the structure of the deposited layers previously, here we present the advantage of using such bi-phasic structures for the laser assisted alumina synthesis first time.

Following the laser treatment, the coalescence of such high aspect ratio structures lead to formation of fractal like structures (Fig. 1b and c). Decreasing the scanning speed from 5 mm/s to 3.2 mm/s (at the same laser fluence of 5.09×10^4 W/cm^2) increases the material–laser interaction time and the densification difference can be easily seen. Depending on the scanning speed, the densification can be controlled easily. We achieved fully densification at a scanning speed of 1.6 mm/s at the same laser fluence. One can decrease the scanning speed in order to get densification at even lower laser energies. The change in the colour of deposited layers from grey-black to white can be related to the morphological change as well as fully oxidation of aluminium (core) to stable alumina phase. Our recent detailed optical characterization showed that Al/Al_2O_3 bi-phasic nanostructures exhibits a broad band absorption, which can be attributed to super positioning of different plasmon modes at different wavelengths due the tangled and interconnected metal–dielectric core–shell nanostructures [16]. As an advantage of high absorption at visible wavelengths, it is possible to induce local phase transformation in sub-micrometre scale (by focusing the laser beam to a much smaller area) in comparison to infra-red wavelength lasers, e.g. CO_2 lasers. As it is clear that use of shorter wavelength lasers will definitely lead to high resolution patterning as a consequence of Abbe diffraction limit.

XRD analysis shows that laser treatment induces an effective phase transformation and crystallization (Fig. 2). One can see the clear crystalline peaks of α-Al_2O_3 phase after the laser treatment, which were absent prior to laser treatment. By increasing the exposure time (lower scanning speed) a decrease in the amount of metallic aluminium is also observed. Simultaneously, increase in the intensity of crystalline peak is seen clearly. At the latest stage, metallic aluminium is totally vanished and the intensity of α-Al_2O_3 peak gets higher. This is a clear evidence of the crystallization and transformation to α-Al_2O_3.

A typical load displacement (L–D) curve during nanoindentation of the sample treated at scanning speed of 1.6 mm/s and a laser fluence of 5.09×10^4 W/cm^2 is shown in Fig. 3. Nanoindentation utilizes continuous measurement of the displacement as the load is applied and then removed. The loading portion of the curve measures the resistance of the material to the penetration. An completely elastically deformed material will retrace the loading curve upon unloading. Oppositely, a primarily plastically deformed material will have almost no elastic recovery. On the other hand, we observed totally different response which can be explained