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Atomic layer deposition as a tool of Surface engineering

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ABSTRACT

The applications of nanostructured materials are close related to their shape and properties. A comprehensive understanding of the properties modification by controlling the material size, thickness or shape is of key importance. A nanostructure can become a building block to create the upcoming nano-technological stages, where the final characteristics of devices can be fine-tuned from design. In this report it is shown that several physicochemical properties, such as refractive index, band gap or thermal resistance can be modified in a controlled fashion. ALD is a very versatile fabrication technique for building nanotubes (Al_2O_3 and TiO_2), nanolaminates (Al_2O_3-ZnO, Y_2O_3-ZrO_2 and ZrO_2-TiO_2) and core-shell materials (diamond-Al_2O_3) with an exquisite precision on the thickness of the coatings.

***Keywords*:** ALD, Surface, Nanolaminates, nanotubes

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1. INTRODUCTION

The surface of a material is the interface by which the material interacts with its environment. The surfaces are fundamental to determine the material properties. Surface engineering involves modifying the composition of the surface to change the properties of a given material. Traditionally, coatings are few micrometers of thickness, but with the advent of nanotechnology, the desired modification can be achieved even by incorporating few atomic layers of the material of choice [1–4].

Numerous coating techniques are currently used, developing in this way a new series of functionalities for the coated material including mechanical, electrical, electronic, magnetic and corrosion resistant properties. It is important to choose an adequate coating technique for the modification of a given surface, which can be able to control the thicknesses and homogeneity of the coatings. There are factors like the geometry of the substrate, the covered area, the rugosity of surface and the interaction between substrate and coating, that are important to consider before selecting the coating technique.

It is imperative for industrial applications that the deposition technique can be scaled for massive production at low cost, being at the same time environmentally friendly. Atomic layer deposition (ALD) is evolving as a very valuable deposition technique since it fits the above requirements. The main advantage is the exquisite precision down to the sub-nanometer scale, independently of the surface geometry [5–7]. It holds tremendous potential across a wide range of industrial applications, including energy, optics, catalysis, electronics, mechanical, magnetic, nanostructures or biomedical applications [8–10]. An ALD cycle corresponds to depositing a slightly under a mono layer of material. Reaction cycles are then repeated until the desired film thickness is reached [5–7]. The choice of materials is critical to fine tune the desired properties, either with minimum disruption of the main functionalities of the base structure or to create a completely new characteristic on the surface.

In this work, we explore the use of ALD in a variety of materials, like powders and flat substrates. We report the surface engineering of selected nanostructures (1D, 2D and grain powders) and demonstrate the potential of ALD to fine tune several properties of relevance for the coated material.

2. EXPERIMENTAL

The coating of the different materials was accomplished on two different ALD systems, depending on the nanostructure shape. Nanotubes (1D) and powders were coated on a home-made fully automated stainless steel pulsed-bed atomic layer deposition hot wall reactor. A description of the original experimental setup can be found elsewhere [1,2]. Powder-like materials in a free-standing state are coated using a porous powder holder placed inside the tubular reactor.

Carrier and purging gas is UHP N2 (10^{-10} ppm O_2). 2D nanostructures (nanolaminates) were deposited on a Beneq TFS 200 viscous-flow reactor at 200 °C on Si (100) substrates. Trimethyl-aluminum (TMA), tetrakis (dimethylamino) titanium (TDMAT), Diethyl Zinc (DEZ) and Tris(methylcyclopentadienyl) yttrium ($(MeCp_3)_3Y$) were the metal precursors and water the oxidizing agent.

3. RESULTS AND DISCUSSION

3. 1. Tunable optical properties

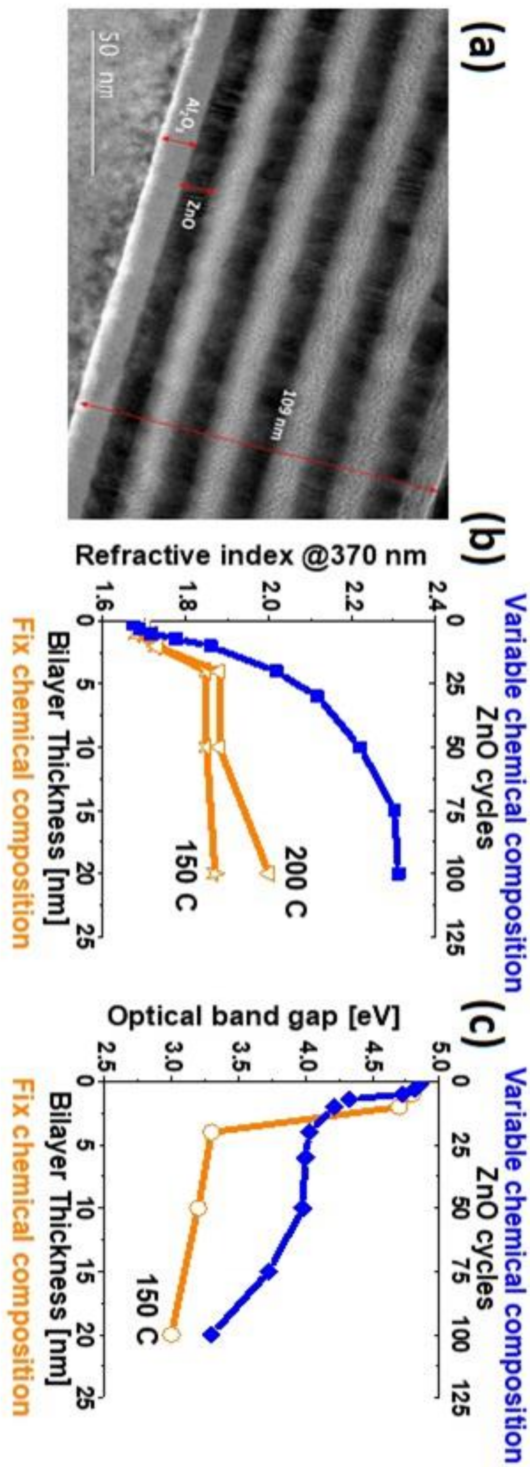

Figure 1. (a) TEM image of Al_2O_3/ZnO nanolaminates. Control of refractive index (b) and optical band gap **(b)** on nanolaminated Al_2O_3:ZnO structures.

The ALD technique makes it possible to fabricate 2D nanostructures by stacking ultrathin films on silicon substrates: nanolaminates (Fig. 1a). These structures allow an accurate control of the optical constants such as the refractive index at the desired chemical composition. For example, nanolaminates (~100 nm total thickness) samples of various chemical composition were built alternating 2nm Al_2O_3 layers with ZnO layers, modifying the ZnO thickness (controlled with the number of ALD ZnO cycles) at different samples. The control of the refractive index is displayed in Fig. 1b.

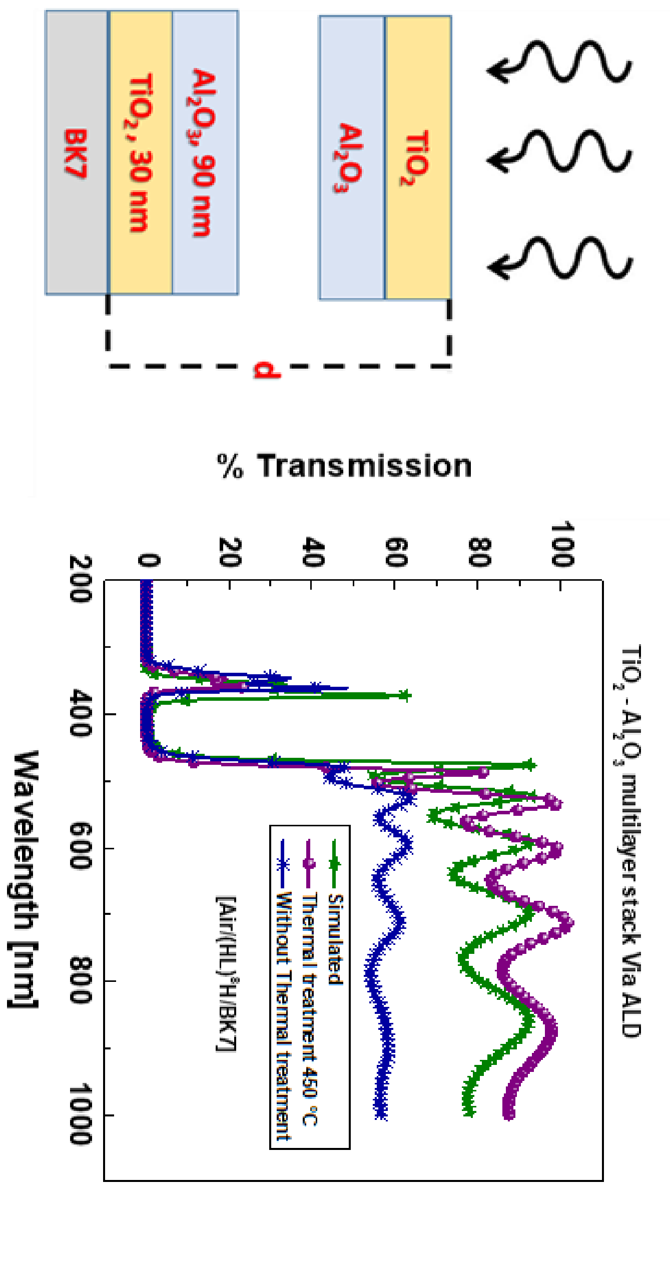

Figure 2. Stack scheme and optical response of an ALD-growth quarter wave TiO_2 - Al_2O_3 multilayer stack. Centered at 410 nm, with stopband region, between 369 - 464 nm.

On the other hand, nanolaminates of constant chemical composition built at 1:1 (Al_2O_3:ZnO) thickness ratio, can modulate its refractive index by means of the bilayer thickness. It can be seen that the deposition temperature has also a slight effect on this property, which can be used for further adjustability. Similarly, a good control of the optical band gap is observed on Fig. 1c as well [3–5].

Multilayer optical filter design was made using an open source code software for interference filters known as ***OpenFilters*** (http://larfis.polymtl.ca/), this program is a powerful tool for design and optimization of optical coatings. The optical coating proposed, was simulated from optical constants $n(\lambda)$ and $k(\lambda)$ obtained for TiO_2 and Al_2O_3 in previous studies using ellipsometric measurements. An ideal model, without surface roughness, and preserving a QW (quarterwave) optical thickness for each layer was applied. The filter was simulated and fabricate over BK7 (**n_s = 1.52**) with stack relation $(HL)^N H$ and based on TiO_2 layers, high refractive index **2.4**, and Al_2O_3 layers, with refractive index **1.67**. In this case optical filter consist of 17 alternating layers with QW stack formula $(HL)^8 H$ and layer thicknesses around ~ 41 nm for TiO_2 and ~ 58 nm for Al_2O_3; this was designed at center wavelength of 410 nm.

It was obtained the transmission for optical coating using a Cary 50 UV-Vis-NIR Spectrophotometer in transmission mode for the wavelength range of 200 – 1100 nm. Fig 2 shows the transmission response for the simulation and experimental data, before and after thermal treatment at 450 °C. In this case we can observe that the as-growth multilayer stack presents a transmittance around ~ 63% before the thermal treatment. The transmittance increases to 98% after the thermal treatment for 1 hour in air. The low transmission can be attributed to residual carbon on the film left by the ALD growing process. The carbon atoms are embedded inside in the multilayer, thereby generating changes in optical properties of the films; these carbon residues can be removed by thermal treatment, as showed in Fig 2.

3. 2. Optical waveguide

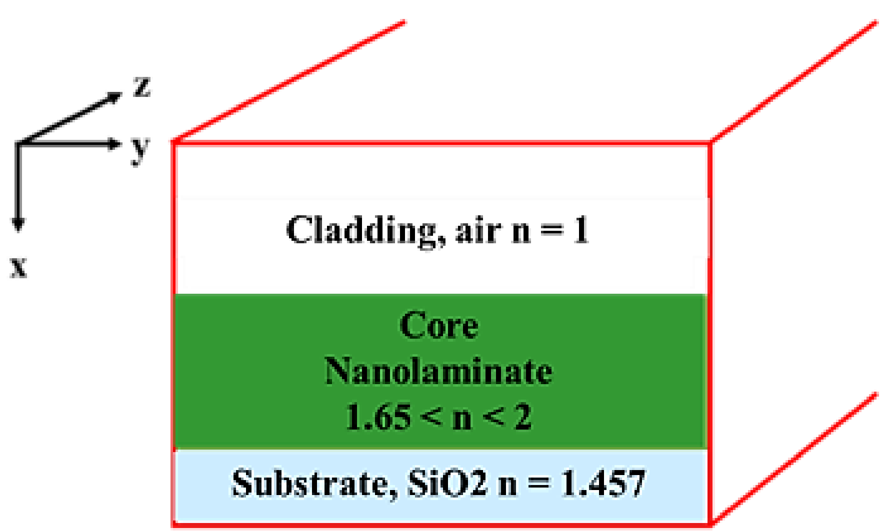

Figure 3. Structure of a slab optical waveguide.

According the results mentioned above, nanolaminates are suited for optical applications like waveguides [5–7]. Fig. 3 shows a slab optical waveguide structure where the core is the nanolaminated structure. The waveguide response is highly dependent of the core refractive index and thickness, therefore modulation at will of the refractive index opens the possibility for the design of waveguides. Moreover, the refractive index contrast between the nanolaminates and the silicon substrate allows designing waveguides of submicrometer core thickness. These structures could be applied as sensors, integrated waveguide devices and hybrid photonic-plasmonic structures [8,9].

3. 3. Particle coatings

(1D Nanostructures). Development of one-dimensional (1D) nanostructures have gained substantial attention over the last 15 –20 years, being the most representative shapes wires, rods, belts and tubes [10,11]. Nanotubes are one of the most attractive 1D nanomaterials as it offers unique physical and chemical properties which translate into promising applications. For example its high surface area can be exploited on photocatalytic devices, material science and medicinal chemistry [12,13]. ALD aided by removable templates facilitates the synthesis of 1D nanostructures. One effective template are the well-known carbon nanotubes (CNTs), which can be synthesized by simple and easily scalable methods [10,14–16]. Inorganic nanotubes can be fabricated by coating CNTs with semiconductor materials, TiO_2 for instance (Fig. 4a) with a homogeneous thickness from 2 to 25 nm [15,16]. Additionally, we found than a thin Al_2O_3 layer serving as a structural component, can improve the structural strength of TiO_2 hollow tubes, after thermal oxidative removal of the CNT core. Moreover, the Al_2O_3 buffer layer prevents the phase transition from anatase to rutile, and therefore the formation of nanocrystal chains, which in turns, collapses the hollow TiO_2 tubes as observed on Fig. 4b.

(Heterostructures 1D). The formation of heterostructures are of key importance in tailoring the energy band diagram characteristics of 1D nanostructures. Titanium oxide or Zinc Oxide are semiconductor materials highly investigated because they are non-toxic, environmentally friendly, and chemically stable. In combination with CNT, which possess high surface to volume ratio, mechanical strength and good electrical conductivity, add to the advantages that the above mentioned semiconductors provide [17]. These structures are suitable for the decomposition of organic pollutants by photocatalysis, because of its strong oxidation ability. However, one of the main drawbacks is the recombination of photo-generated electron-holes pair. Recently, the semiconductor-semiconductor (S-S) hetero-junction has also been confirmed as an effective approach to reduce this issue [18]. One of the main task in our group is coating the carbon nanotubes with a S-S shell in order to improve the photocatalytic performance (Fig. 5).

(Powder coating and thermal oxidation protection). Synthetic diamond powders are utilized for cutting, grinding and shaping hard and abrasive materials due their high mechanical hardness. However, its limited resistance to oxidation at high temperatures (>500 C) has hindered the number of applications [19]. To improve the thermal resistance of diamond powder, it was coated with aluminum oxide by ALD to protect the particles from ambient oxygen (Fig.6) [20]. The results show that the protected surface of diamond can be withstands higher temperatures in air. Even when the improvement is modest, the oxidation rate is actually slowed down for about 3 times, compared to the uncoated diamond.

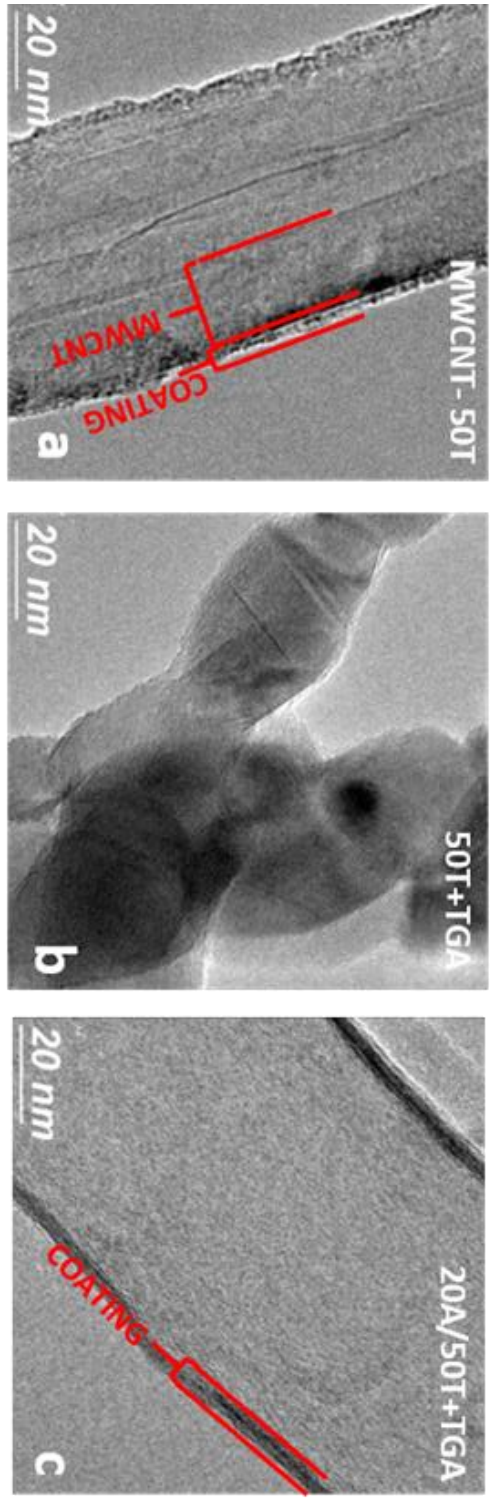

Figure 4. TEM images of MWCNTs coated with 50 TiO_2 ALD as deposited (a) and after template removal (b). To avoid the collapse from tubular structure were employed an Al_2O_3 buffer layer (c).

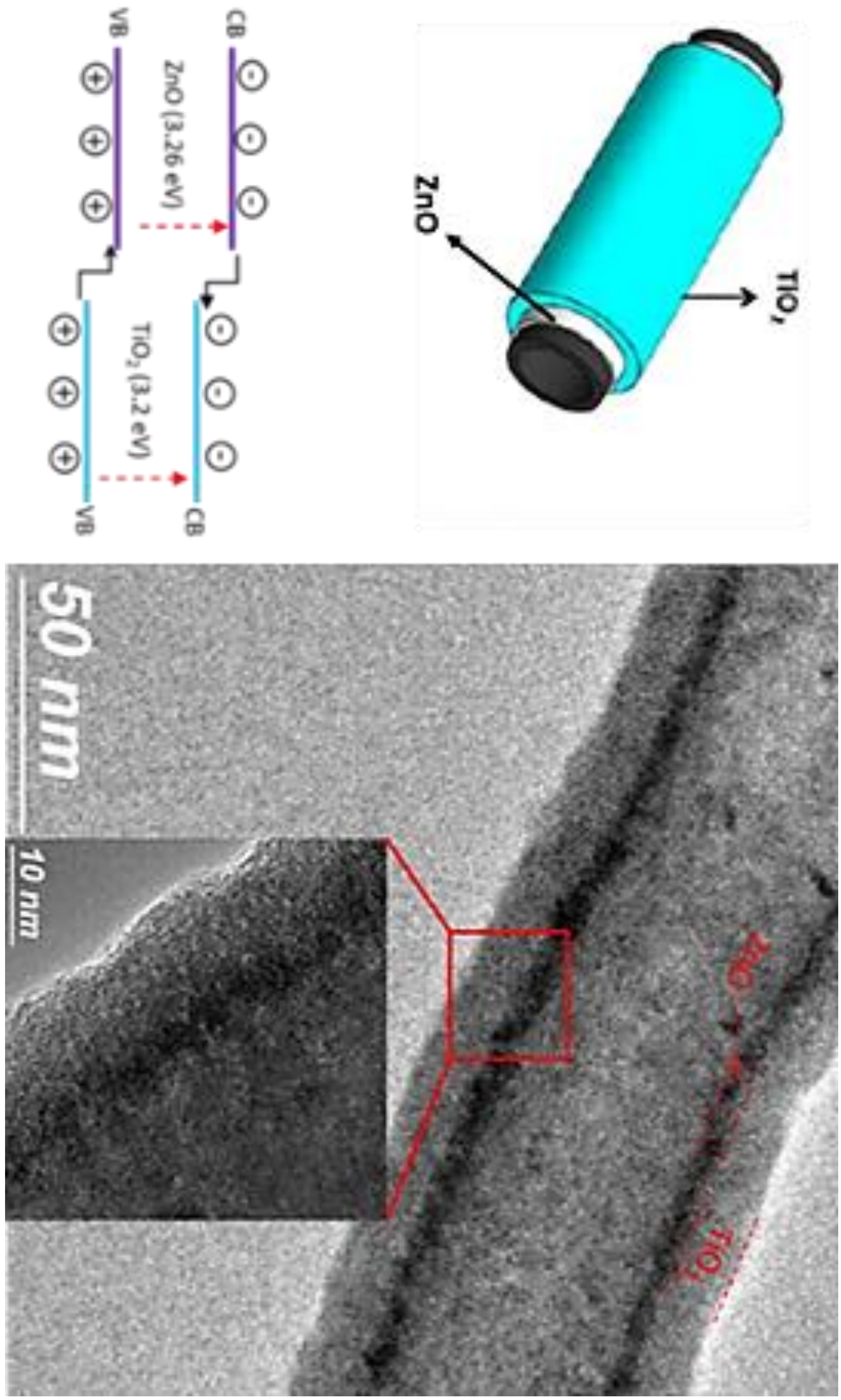

Figure 5. Schematic representation of the S-S nanostructure and the band energy of the electron-hole separation. Also, a TEM image of a nanotube coated with TiO_2 and ZnO.

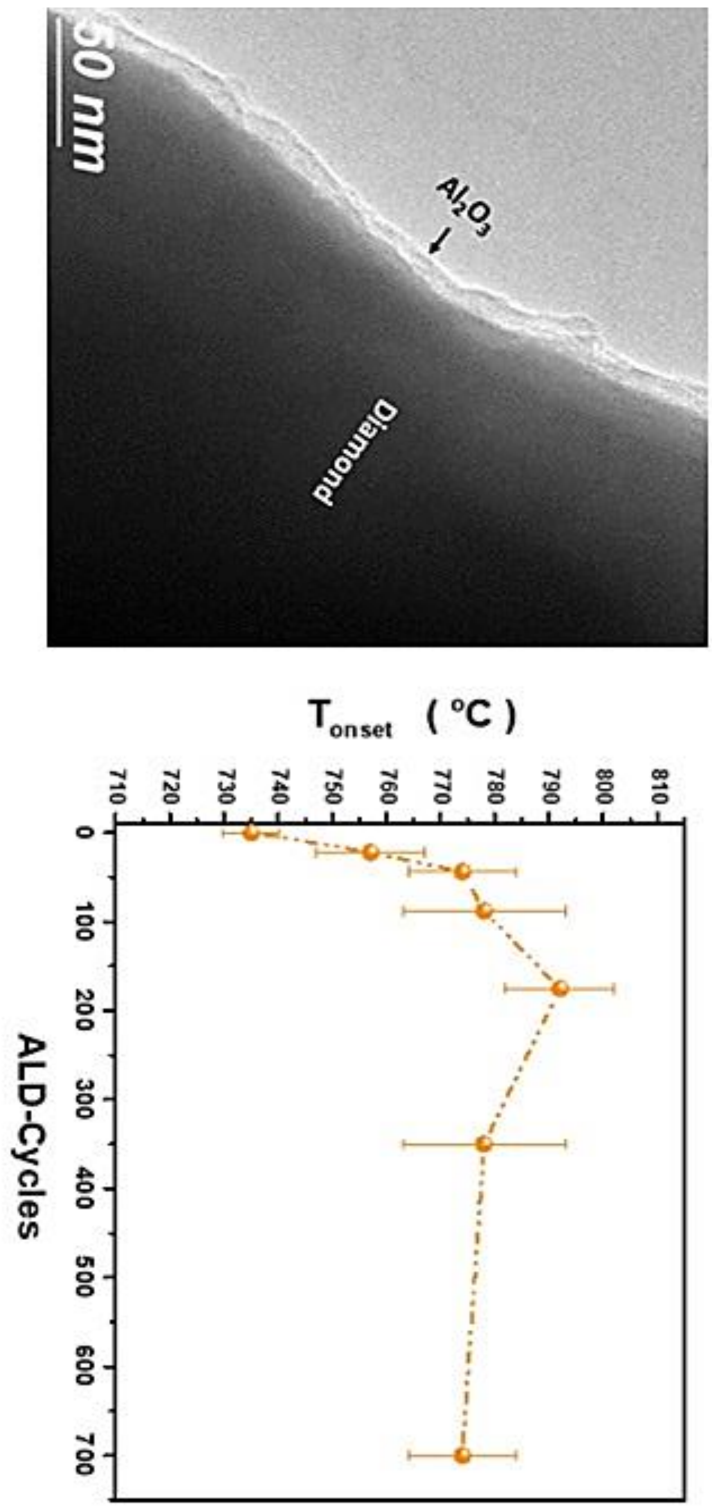

Figure 6. TEM image of Al_2O_3 coating of diamond powder, and temperature of degradation of diamond powder (Tonset) in dry air as a function of ALD cycles.

4. CONCLUSIONS

The surface engineering approach by means of ALD are found to be a real-world path for fabrication of well controlled nanostructures on flat, complex surfaces and high surface area nanostructures, in a conformal and homogeneous manner, with a precise control of a few nanometers on thickness that effectively adjusts properties of key importance.

Acknowledgments

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