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Influence of coating and annealing on the luminescence of Ga_2O_3 nanowires

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Ga_2O_3-core/CdO-shell nanowires were synthesized by a two step process comprising thermal evaporation of GaN powders and sputter-deposition of CdO. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analyses revealed that the cores and the shells of the annealed coaxial nanowires were single crystal of monoclinic Ga_2O_3 and FCC CdO, respectively. As-synthesized Ga_2O_3 nanowires showed a broad emission band at approximately 460 nm in the blue region. The blue emission intensity of the Ga_2O_3 nanowires was slightly decreased by CdO coating, but it was significantly increased by subsequent thermal annealing in a reducing atmosphere. The major emission peak was also shifted from ~500 nm by annealing in a reducing atmosphere, which is attributed to the increases in the Cd interstitial and O vacancy concentrations in the cores.

Key words: Ga_2O_3 nanowires, Thermal evaporation, CdO coating, Photoluminescence, Annealing.

Introduction

Monoclinic gallium oxide (β-Ga_2O_3) is one of the important wide band-gap semiconductor (E_g = ~4.9 eV) with good chemical and thermal stability [1]. This material has been studied for applications in ultraviolet luminescence, high temperature gas sensors, phosphors, transparent conducting electrodes, dielectric gates, and high temperature gas sensors [2-5]. Recently, one-dimensional (1D) nanostructures are the subject of intensive research due to their potential for nanoscale electronic and optoelectronic applications. A common technique to control and enhance the properties of the 1D nanostructures is to create core-shell heterostructures [6, 7]. This work represents the structure and PL properties of Ga_2O_3-core/CdO-shell nanowires to give an insight in tailoring the optical properties of Ga_2O_3 nanowires and to elucidate the complicated dependence of the PL properties on the coating material and annealing atmosphere. Ga_2O_3 nanowires were synthesized first by using thermal evaporation of GaN powders because it is easiest and offers nanowires with a relatively good quality. Next, a radio-frequency (RF) magnetron sputtering technique was used to form CdO shells on Ga_2O_3 cores. Various techniques have been reported to be used to form shell layers on the nanowire cores. These techniques include sol-gel process, thermal heating, solution-based method, and chemical vapor deposition (CVD) [8-10]. Sputtering is known to be a much simpler deposition technique than CVD but to offer thickness uniformity worse than CVD. Nevertheless, it was found that the thickness uniformity of the CdO shell layers formed on the Ga_2O_3 cores by sputtering was much better than expected.

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Experimental

Gold (Au)-coated Si were used as substrates for the synthesis of 1D Ga_2O_3 structures. Au was deposited on the (100) Si substrate by RF magnetron sputtering. A quartz tube was mounted horizontally inside a tube furnace. The 99.99% pure GaN powders were placed on the lower holder at the center of the quartz tube. The Au-coated Si substrate was placed on the upper holder about 5mm apart from the GaN powders. The furnace was heated up to 1050 °C and maintained at the temperature for 1 h in N_2/3 mol%-O_2 atmosphere with constant flow rates of oxygen (15 standard cubic centimeter per minute (sccm)) and nitrogen (485 sccm). The total pressure was set to 1.5 torr. Next, the substrates were transferred to a RF magnetron sputtering system for CdO coating. The sputtering was performed at room temperature for 15 min using a 99.95% CdO target. The sputtering process parameters for the CdO deposition used in the sputtering process are as follows: RF power of 100 W, base vacuum of 1.0×10^{-6} torr, chamber pressure of 1.8×10^{-2} torr, Ar gas flow rate of 30 sccm, and substrate temperature of room temperature. After CdO coating, the products were annealed at 650 °C for 1 h in an O_2 or N_2/3 mol%-H_2 atmosphere. The process parameters for the annealing were as follows: (O_2 annealing) O_2 flow rate of 200 sccm, base pressure of 2.5×10^{-2} torr, and chamber pressure of 0.8 torr; (N_2/H_2 annealing) N_2/3 mol%-H_2

mixed gas flow rate of 100 sccm, base pressure of 2.5 $\times 10^{-2}$ torr, and chamber pressure of 0.1 torr.

The products were then characterized using glancing angle (0.5 °) XRD (X'pert MPD-Philips with Cu-Ka radiation), scanning electron microscopy (SEM, Hitachi S-4200), and TEM (Phillips CM-200). The high resolution TEM (HR-TEM) images and the selected area electron diffraction (SAED) patterns were also taken on the same systems. The compositional analysis was done by using an energy dispersive X-ray spectroscope (EDXS) installed in the TEM. Photoluminescence (PL) measurements were performed at room temperature in a SPEC-1403 PL spectrometer with a He-Cd laser line of 325 nm as the excitation source (Kimon, 1 K, Japan).

Results and Discussion

Fig. 1(a) shows the SEM image of the β-Ga_2O_3 nanowires synthesized. Most of the nanowires have a rod-like morphology. The rod-like nanostructures look quite uniform in diameter. The EDX spectrum (Fig. 1(b)) of the Ga_2O_3-core/CdO-shell nanowires indicates that the nanowires comprise only Ga, O, and Cd as well as Au used as a catalyst without any impurity such as N which might originate from GaN powder that was the source material for Ga_2O_3 nanowire synthesis. Most nanowires have diameters ranging from a few tens to a few hundreds of nanometers and lengths of a few micrometers as shown in a typical nanowire in the inset of Fig. 1. Most nanowires have a globular particle at their tips with a diameter larger than those of the other parts of the nanowires, suggesting that the growth mechanism of the nanomaterials can be regarded as a vapor-liquid-solid (VLS) mechanism. Figs. 2(a) and (b), respectively, show the XRD patterns of as-synthesized and annealed nanowires. The main diffraction peaks in the pattern of the as-synthesized core-shell nanowires (Fig. 2(a)) fit to a monoclinic β-Ga_2O_3 crystals (JCPDS card No. 43-1012, a = 12.23 Å, b = 3.04 Å, c = 5.80 Å, β = 103.7 °). No appreciable CdO reflection peak is

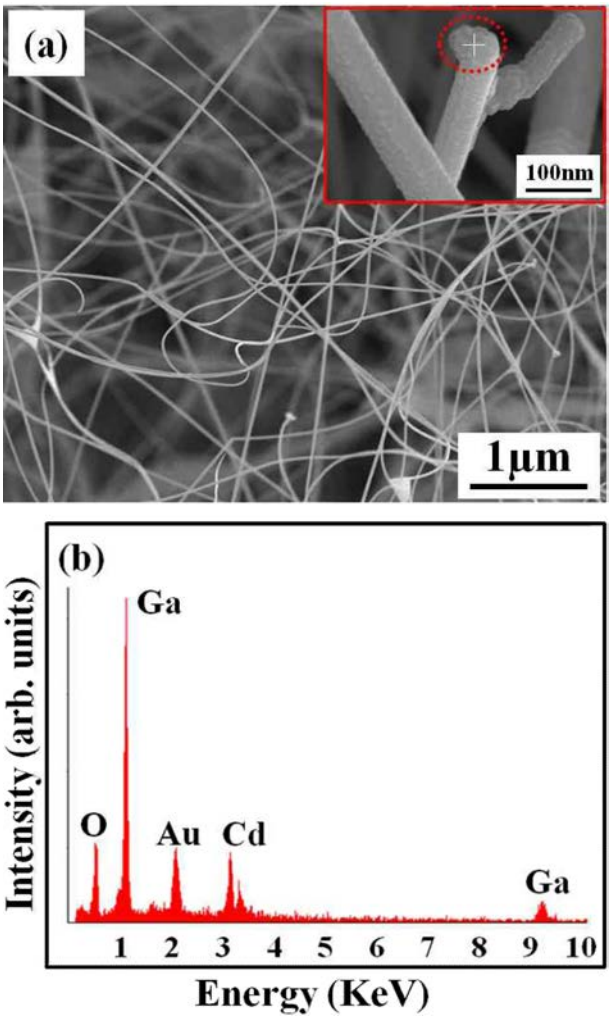

Fig. 1. (a) SEM image of Ga_2O_3/CdO coaxial nanowires. Inset, the catalyst particle at the tip of a nanowire and (b) EDX spectra taken from the particle at the tip of a Ga_2O_3/CdO coaxial nanowire in the inset of Fig. 1(a).

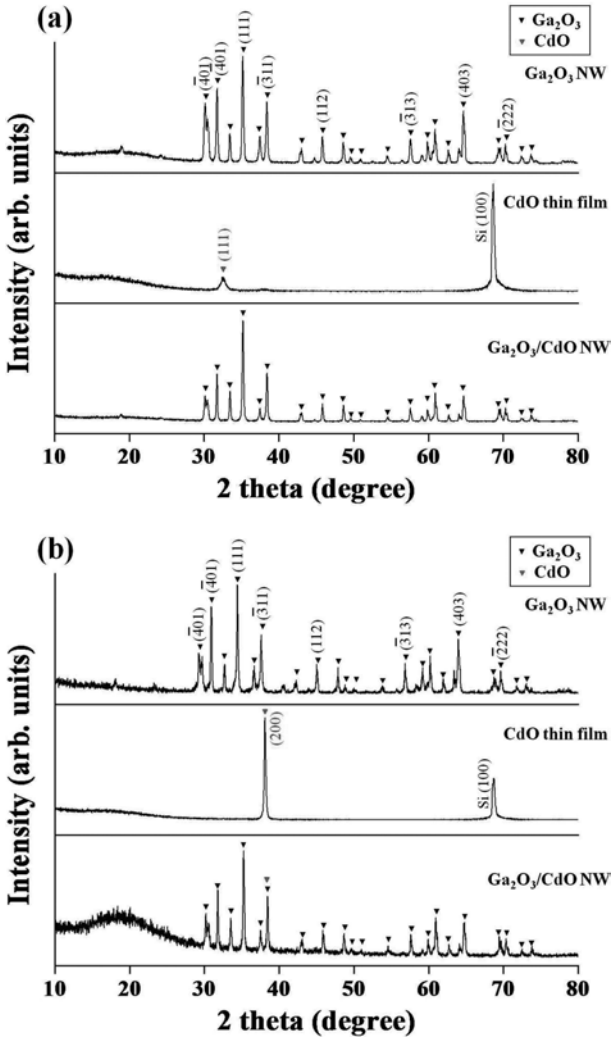

Fig. 2. XRD patterns of (a) the as-synthesized and (b) annealed Ga_2O_3 nanowires, CdO thin films (corresponding to CdO shells), and Ga_2O_3/CdO coaxial nanowires.

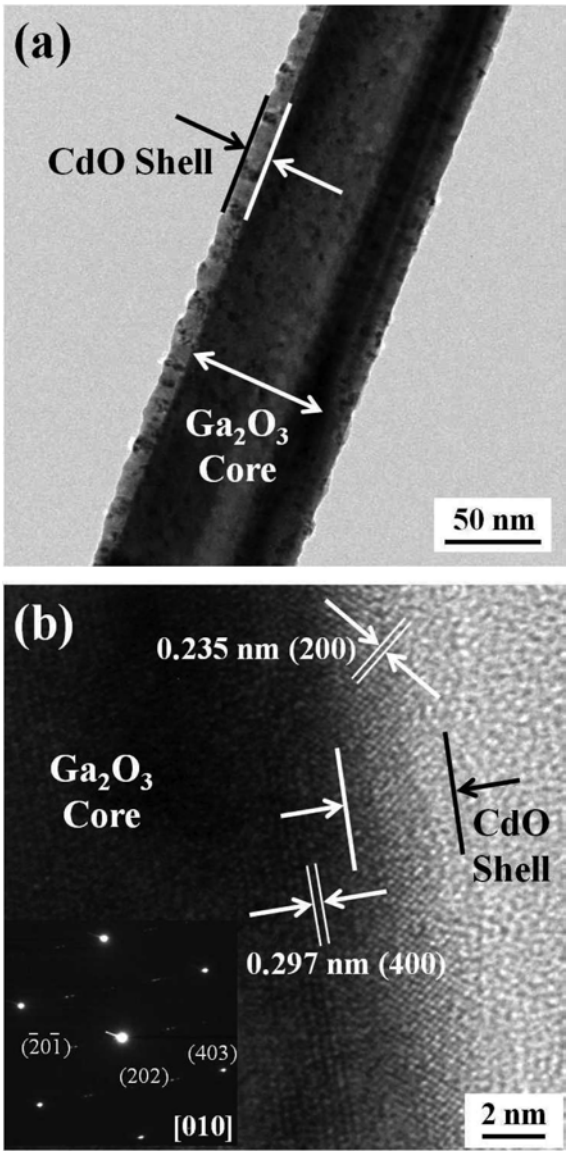

Fig. 3. (a) Low-magnification TEM image of a typical Ga_2O_3/CdO coaxial nanowire. (b) Local HR-TEM image of the nanostructure at the core-shell interface region and inset image represents corresponding SAED pattern with the [010] zone axis.

observed for as-synthesized core-shell nanowires, suggesting that the as-sputtered CdO shell layers are amorphous. In contrast, the (200) reflection peak for a CdO phase as well as the reflection peaks for β-Ga_2O_3 exist in the diffraction pattern of the annealed core-shell nanowires (Fig. 2(b)), suggesting that the CdO shells have been crystallized by thermal annealing.

Fig. 3(a) shows a low-magnification TEM image of a typical annealed core-shell nanowire, revealing that indeed a core-shell structure with a shell thickness of 10-15 nm, indicating that the thickness uniformity of the CdO shell is relatively good despite having been formed by sputter-deposition which is a typical physical vapor deposition technique. A local HR-TEM image enlarging the core-shell interface region of a typical core-shell nanowire is shown in Fig. 3(b). The

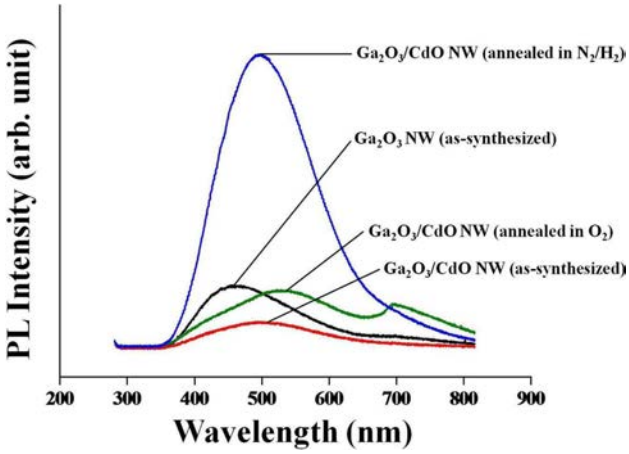

Fig. 4. Room temperature-PL spectra of the Ga_2O_3/CdO coaxial nanowires annealed at 650 °C for 30 min in different atmospheres along with as-synthesized Ga_2O_3 and Ga_2O_3/CdO coaxial nanowires.

resolved spacing between two neighboring parallel fringes in the core region was about 0.297 nm corresponding to monoclinic β-Ga_2O_3 (400) plane, whereas that between two neighboring parallel fringes in the shell was about 0.235 nm corresponding to face-centered cubic (FCC) CdO (200) plane. The associated SAED pattern (inset of Fig. 3(b)) recorded perpendicular to the long axis was indexed for the [010] zone axis of β-Ga_2O_3. Close examination indicates that there is a weak diffraction pattern for the FCC CdO phase besides a clear pattern for the monoclinic β-Ga_2O_3 phase. The SAED pattern as well as the TEM image verifiy that both the core and the shell of the annealed core-shell nanowires are monocrystalline.

Fig. 4 displays the PL spectra, measured at room temperature, of the Ga_2O_3-core/CdO-shell nanowires annealed in different annealing atmospheres along with as-synthesized Ga_2O_3 nanowires and Ga_2O_3-core/CdO-shell nanowires. The PL spectrum of the as-synthesized Ga_2O_3 nanowires is characterized by an emission band centered at approximately 460 nm. This emission was reported to be associated with the vacancies in the Ga_2O_3 cores, such as gallium (Ga) vacancies, oxygen (O) vacancies [11] and Ga-O vacancy pairs [12]. Binet and Gourier [14] reported that this emission could be produced by the tunnel recombination of an electron on a donor with a hole on an acceptor which could be either a Ga vacancy or a charged Ga or O vacancy. Vacancies seem to be easily generated as the Ga_2O_3 nanowires were synthesized by the thermal evaporation of GaN powders at a temperature as high as 1050 °C in this work. The PL emission of Ga_2O_3 nanowires has been slightly degraded in intensity and red-shifted to ~500 nm (the blue-green region) by CdO coating. The decrease of the emission intensity might be caused by the absorption of the light, emitted from the Ga_2O_3 core, by the CdO shell before it reaches our eyes since the CdO shell layer is not highly transparent.

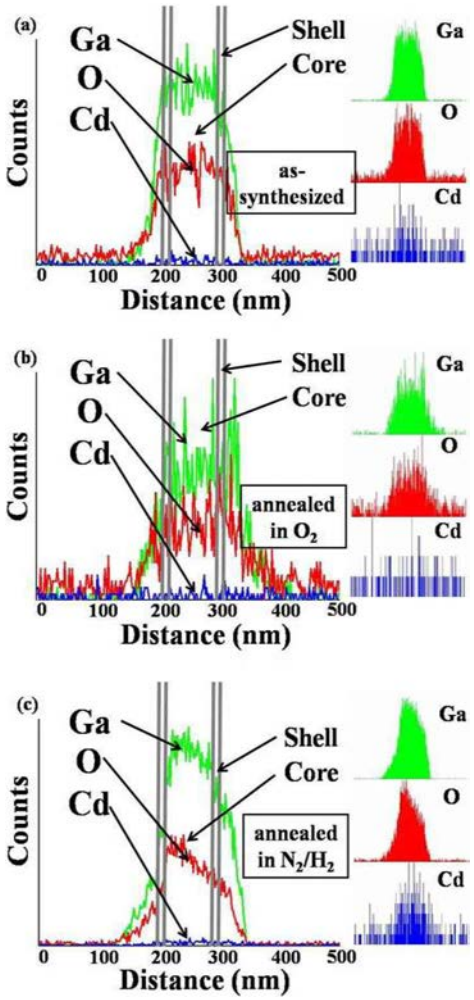

Fig. 5. EDXS line scanning concentration profiles of the Ga_2O_3/CdO coaxial nanowires: (a) as-synthesized (un-annealed), (b) annealed in an O_2 atmosphere, and (c) annealed in a N_2/H_2 atmosphere.

On the other hand, the PL emission of the Ga_2O_3-core/CdO-shell nanowires was slightly enhanced in intensity and the emission peak was shifted from ~500 to ~520 nm (the green region) by subsequent thermal annealing in an O_2 atmosphere. In contrast, it was significantly enhanced in intensity without a shift of the emission peak by annealing in an N_2/H_2 atmosphere. We performed EDXS analysis to examine the origin of the PL enhancement and the red-shift by annealing. The EDXS concentration profile of the Ga_2O_3-core/CdO-shell nanowires annealed in an O_2 atmosphere (Fig. 5(b)) compared with that of the as-synthesized Ga_2O_3 nanowires (Fig. 5(a)) reveals that the concentration ratio of O/Ga in the Ga_2O_3 core region has increased after O_2 annealing. The increase in the oxygen (O) concentration in the cores, in turn, leads to the decrease in the O vacancies and, furthermore, the increase in the concentrations of O interstitials or Ga vacancies, resulting in the enhancement of the green emission. In contrast, the oxygen vacancy and Ga interstitial concentrations in the Ga_2O_3 core are increased by annealing in the N_2/H_2 atmosphere, which results in the enhancement of the deep level-related emission in intensity. Close comparison of the EDXS concentration profile of the Ga_2O_3-core/CdO-shell nanowires annealed in a N_2/H_2 atmosphere (Fig. 5(c)) with that of the as-synthesized nanowires (Fig. 5(a)) indicates that the concentration ratio of O/Ga in the Ga_2O_3 core region has decreased after N_2/H_2 annealing. It is well known that oxygen vacancies are formed in Ga_2O_3 under reduction growth conditions, forming an n-type semiconductor. Post-annealing of Ga_2O_3 nanostructures in a reduction atmosphere also appears to generate oxygen vacancies and thus to enhance the luminescence intensity significantly.

Harwig *et al.* [11] showed that samples annealed in a reduction atmosphere were in favor of formation of O vacancies and blue emission was enhanced, while the samples heated in an O_2 atmosphere were in favor of formation of Ga vacancies, which showed a dominant green emission. Villora *et al.* [14] reported that with the decease of the O_2 partial pressure, the cathodoluminescence emission decreased in intensity, and shifted from the green region to the blue region. Our results are in good agreement with the previous reports in that the PL emission was increased in intensity and shifted to the

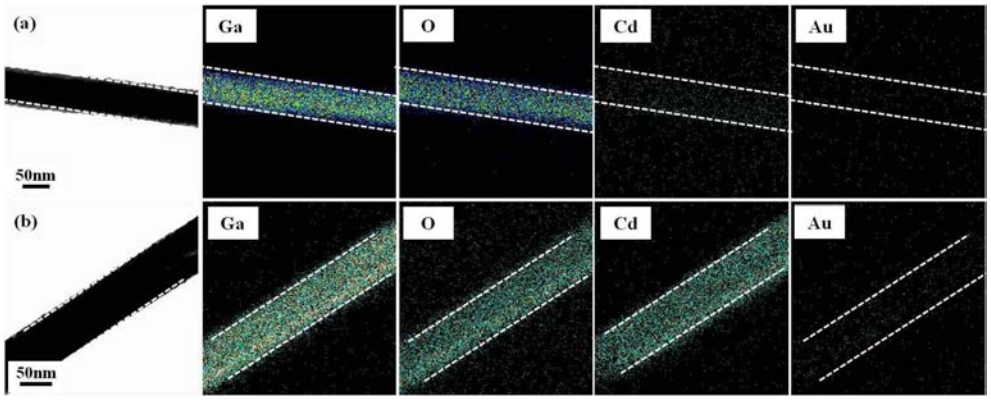

Fig. 6. EDXS elemental maps of the Ga_2O_3/CdO coaxial nanowires: (a) as-synthesized (un-annealed), and (b) annealed in a N_2/H_2 atmosphere.

green region by annealing in an O_2 atmosphere.

Another notable change might have occurred during the annealing process in the H_2/N_2 atmosphere. The Ga_2O_3 cores might not have been spontaneously dissociated by reacting with H_2, but the CdO shell layers might have been dissociated as follows [15]:

$$Ga_2O_3(s) + 3H_2(g) = 2Ga(s) + 3H_2O(g): \Delta G_{f,\,873K} = 204.463\ KJ/mol \quad (1)$$

$$CdO(s) + H_2(g) = Cd(s) + H_2O(g): \Delta G_{f,\,873K} = -29.21303\ KJ/mol \quad (2)$$

Comparison of the Cd elemental map between before and after annealing in N_2/H_2 atmosphere (Fig. 6 (a) and (b), respectively) clearly indicates that Reaction 2 has occurred during the annealing process. It is evident that the Cd concentration in the nanowires after annealing is substantially higher than that before annealing. It is also very likely that the extra Cd atoms produced as a result of Reaction 2 diffused into the Ga_2O_3 core during the annealing process and resided at the interstitial sites, which might have made a significant contribution to the enhancement of the blue-green emission as well as the O deficiency.

Conclusions

The Ga_2O_3-core/CdO-shell nanowires were prepared by a two step process of thermal evaporation of GaN powders and sputter-deposition of CdO. The cores and shells of the annealed core-shell nanowires were monoclinic Ga_2O_3 and FCC CdO single crystal, respectively. SEM and TEM images of the core-shell nanowires showed that uniform coating of nanowires could be achieved by using a sputtering technique despite its being a typical physical vapor deposition technique. As-synthesized Ga_2O_3 nanowires showed a broad emission band at approximately 460 nm in the blue region. The major PL emission intensity of Ga_2O_3 nanowires was slightly decreased by CdO coating. The PL emission intensity of Ga_2O_3 nanowires was slightly increased and the emission peak was shifted from 500 nm to ~520 nm by subsequent thermal annealing in an oxidizing atmosphere. The O concentration in the Ga_2O_3 core regions increased significantly during O_2 annealing, leading to increases in the O interstitial and Ga vacancy concentrations and resulting in the enhancement in the green emission. In contrast, the PL emission of the wires was increased significantly and the emission peak was shifted from 500 nm by annealing in a reducing atmosphere, presumably originating from the increases in the O vacancy and Ga interstitial concentrations in the Ga_2O_3 core as a result of the reaction between Ga_2O_3 and H_2. The results obtained in this study will give an insight in tailoring the optical properties of semiconductor nanostructures by means of coating and thermal annealing.

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