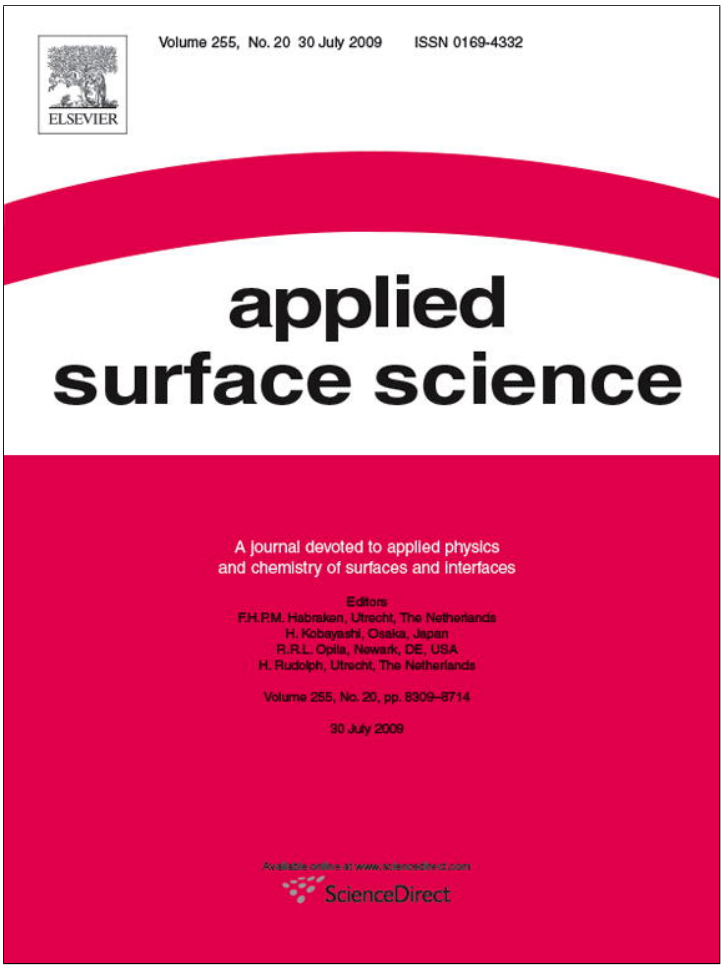

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Co-sheathed SiO_x nanowires

Hyoun Woo Kim [a,*], Hyo Sung Kim [a], Mesfin Abayneh Kebede [a], Han Gil Na [a], Ju Chan Yang [a], Yong Sung Koo [b], Jong Hoon Jung [b], Nam Jung Hur [b]

[a] Division of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea
[b] Department of Physics, Inha University, Incheon 402-751, Republic of Korea

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ABSTRACT

We fabricated Co-coated SiO_x nanowires and investigated the effects of thermal annealing on their properties. The sputtering process resulted in the formation of a relatively smooth Co shell layer, whereas subsequent thermal annealing generated the Co_3O_4 phase. The photoluminescence (PL) spectrum was not changed by the Co-coating, whereas the thermal annealing induced new peaks in the yellow and ultraviolet regions. Possible emission mechanisms were discussed. Based on the magnetization measurements of the SiO_x-core/Co-shell nanowires, we obtained small and negligible hysteresis loops for the as-fabricated and thermal annealed samples, respectively.

1. Introduction

Owing to their intriguing properties and potential applications in optics, electrics and optoelectronics, one-dimensional (1D) nanostructured materials have attracted extensive research interest [1–3]. Moreover, the fabrication of coaxial nanocables will modify or improve the properties of the individual materials. Accordingly, the fabrication and properties of core-shell nanowires have been intensively studied [4,5].

Silicon oxide (SiO_x) nanowires have potential applications in mesoscopic research, high-resolution optical heads, nano-scale optical devices, and catalyst [6–8]. Also, they have been used as insulating core materials for fabricating core-shell nanowires [4]. On the other hand, metal nanostructures have attracted considerable attention from scientists and engineers on account of their application to many areas of fundamental and technical importance [9]. Among the various metallic nanostructures, cobalt (Co) nanowires have attracted much interest in recent years, due to their remarkable behavior which makes them useful for applications in the field of magnetic storage [10–12] and field emission [13]. Also, Co–SiO_2 nanocomposites are particularly attractive as supported Co catalysts for Fischer–Tropsch synthesis, i.e. the conversion of synthetic gas to long-chain hydrocarbons [14,15].

In this study, we sputtered a Co layer onto as-fabricated SiO_x nanowires, thereby realizing the fabrication of SiO_x-core/Co-shell nanowires for the first time. The capability of fabricating ultrathin Co shell layers on core SiO_x nanowires will provide an opportunity to explore their peculiar and attractive properties. In addition, we annealed the core-shell nanowires and investigated the resultant changes in their physical and chemical properties. In the present study, Co_3O_4 nanoparticles were fabricated on core SiO_x nanowires via thermal annealing. Co_3O_4 nanoparticles have been involved in many advanced chemical and physical applications including catalysis, sensors, magnetic materials, and energy storage [16–20]. Furthermore, Co_3O_4 nanowires have excellent properties for use as anodes in Li ion batteries [21].

2. Experimental

Similar to a previous study [22], the core SiO_x nanowires were fabricated using a tube furnace, in which the Ag (10 nm)-coated Si substrates were heated at 1000 °C for 2 h. Subsequently, the samples were sputtered at room temperature in a turbo sputter coater (Emitech K575X, Emitech Ltd., Ashford, Kent, UK) [23], by

* Corresponding author. Tel.: +82 32 860 7544; fax: +82 32 862 5546.
E-mail address: hwkim@inha.ac.kr (H.W. Kim).

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using a circular Co target. The DC sputtering current was set to 65 mA, and the sputtering was carried out in high-purity argon (Ar) gas flow for 1 min. The as-fabricated samples were annealed for 10 min at 500 °C in air ambient.

The sample morphology was examined by field emission scanning electron microscopy (FESEM) (S-4200, Hitachi). The crystallinity of the nanostructure was analyzed by glancing incident angle X-ray diffraction (GIAXRD) (Philips X'pert MRD diffractometer) with a fixed incident angle of 0.5°. The transmission electron microscopy (TEM) experiments were performed on a CM-200 (Phillips) operated at 200 kV. The photoluminescence (PL) spectrum was obtained at room temperature using an Acton Research spectrophotometer excited by a He–Cd laser (325 nm) in the UV region. Magnetization measurements were performed by means of the vibrating sample magnetometer (VMS) option in a physical property measurement system (PPMS) at room temperature.

3. Results and discussion

Fig. 1a shows the XRD pattern of the as-synthesized SiO_x-core/Co-shell nanowires prior to thermal annealing. Besides the Si (2 0 0) peak and Si (4 0 0) peak presumably originating from the substrate, it is noteworthy that a prominent peak appeared, corresponding to the (2 0 0) reflection of the cubic structure of Co with a lattice constant of a = 3.5447 Å (JCPDS File No. 15-0806). On the other hand, Fig. 1b shows the XRD pattern of the annealed SiO_x-core/Co-shell nanowires. The annealing temperature was set to 500 °C. Apart from the discernible peak of Co (2 0 0), most of the peaks correspond to the reflection of the cubic structure of Co_3O_4 with a lattice constant of a = 8.0840 Å (JCPDS File No. 09-0418). Accordingly, it can be inferred that the Co_3O_4 associated peaks appear as a result of the thermal annealing.

Fig. 2a and b shows the SEM and TEM images of the as-fabricated SiO_x-core/Co-shell nanowires, respectively. Since the nanowires exhibit a relatively smooth surface without any cluster-like or branched structures on their surface, we can suppose that the sputtering was carried out in such a manner to result in a uniform shell layer. Being similar to the SiO_x-coating process by Si sputter target, we surmise that the present Co-coating process is a layer or Frank-van der Merwe growth process [23]. However, it is very difficult for Co shell layer to completely coat on the surface of SiO_x nanowires which lay down on the substrate. The inset of Fig. 2b shows the associated selected area electron diffraction (SAED) pattern. The pattern shows weak diffraction rings, corresponding to the (1 1 0) and (1 1 1) planes of cubic Co. Fig. 3 shows an enlarged TEM image of an as-fabricated SiO_x-core/Co-shell nanowire. Close examination reveals that most of the region is composed of an amorphous structure, due to the absence of lattice images, but some crystalline structures are locally present. The interplanar spacings are approximately 0.20 nm, which is consistent with the (1 1 1) plane of cubic Co.

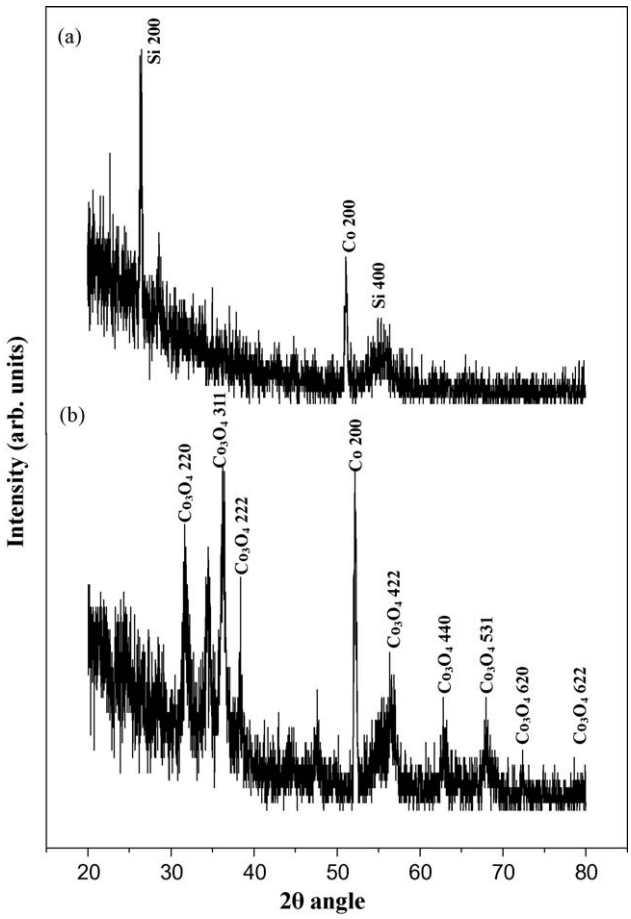

Fig. 1. XRD patterns of (a) as-synthesized and (b) SiO_x-core/Co-shell nanowires annealed at 500 °C.

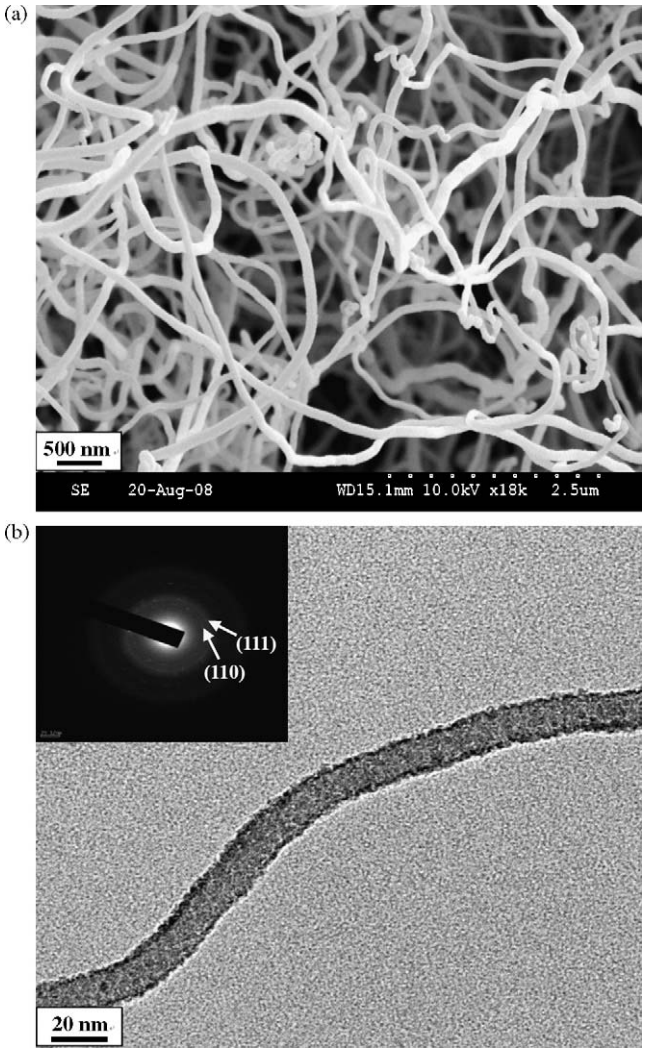

Fig. 2. (a) SEM image of as-synthesized SiO_x-core/Co-shell nanowires. (b) TEM image of an as-synthesized SiO_x-core/Co-shell nanowire (inset: corresponding SAED pattern).

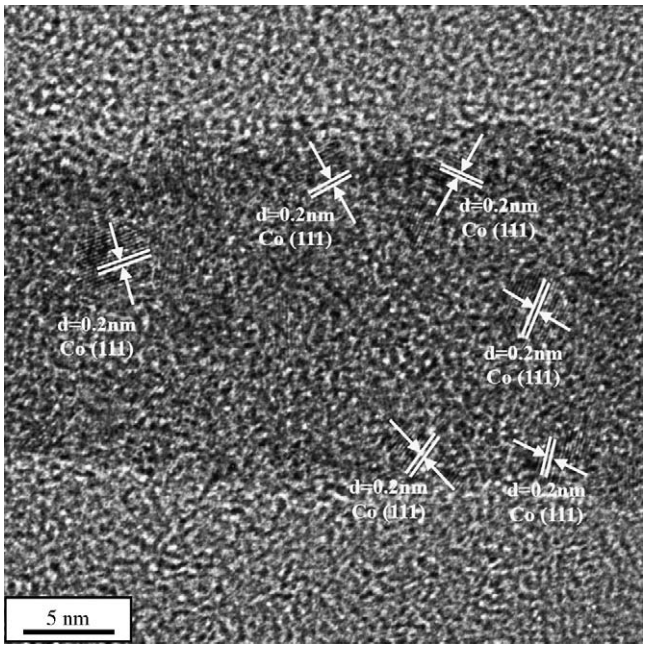

Fig. 3. Enlarged TEM image of an as-synthesized SiO_x-core/Co-shell nanowire.

Fig. 4a and b shows the SEM and TEM images of the SiO_x-core/Co-shell nanowires annealed at 500 °C. The annealed nanowires clearly exhibit a rough surface. By comparing Fig. 4b with Fig. 2b, we surmise that the thermal annealing changed the surface morphology, presumably resulting in the agglomeration of the Co shell layer. Fig. 4c shows the corresponding SAED pattern, which appears to be the superposition of the single crystal spot patterns arising from the polycrystalline nature. The diffraction rings correspond to the reflections of the (2 2 0), (3 1 1), (2 2 2), (5 1 1), (5 3 3), (6 2 2), and (6 4 2) planes of the cubic Co_3O_4 structure. Fig. 5 shows an enlarged TEM image of an SiO_x-core/Co-shell nanowire annealed at 500 °C. Although some regions are amorphous, it is noteworthy that the remaining part is crystalline. The spacings of the adjacent lattice planes are 0.24 and 0.28 nm, which are consistent with the separation of the Co_3O_4 (3 1 1) and (2 2 0) crystal planes, respectively.

The PL spectrum of the SiO_x nanowires prior to the Co coating is shown in Fig. 6a. By Gaussian deconvolution analysis, we found two main peaks at 2.65 and 3.10 eV, in addition to the weak peak at 1.65 eV. It is known that the band at around 2.7 eV can be attributed to the neutral oxygen vacancy, whereas the 3.1 eV-band is due to twofold coordinated silicon lone-pair centers [24,25]. Also, the red emission in silica was assigned to the nonbridging oxygen hole centers [24,26,27]. Fig. 6b shows the PL spectrum of the as-synthesized SiO_x-core/Co-shell nanowires. Since the spectrum is nearly identical to that of the core SiO_x nanowires, we suppose that the Co shell did not contribute to the observed emission. Fig. 6c shows the PL spectrum of the SiO_x-core/Co-shell nanowires annealed at 500 °C. Apart from the three bands originating from the SiO_x-core, the thermal annealing induced two new bands, whose peaks are observed at 2.1 and 3.35 eV, respectively. The 2.1 eV-band is very close to the direct optical bandgap of 2.10 eV for Co_3O_4 thin films [28–30]. The 3.35 eV-band is in the ultraviolet (UV) region and UV light emission has been observed from oxidized porous silicon and SiO_2 powders [31], being ascribed to excess oxygen defects [32]. Since the thermal annealing in the present study was carried out in air ambient, we surmise that oxygen could have been introduced into the SiO_x nanowires, thereby resulting in the 3.35-eV band.

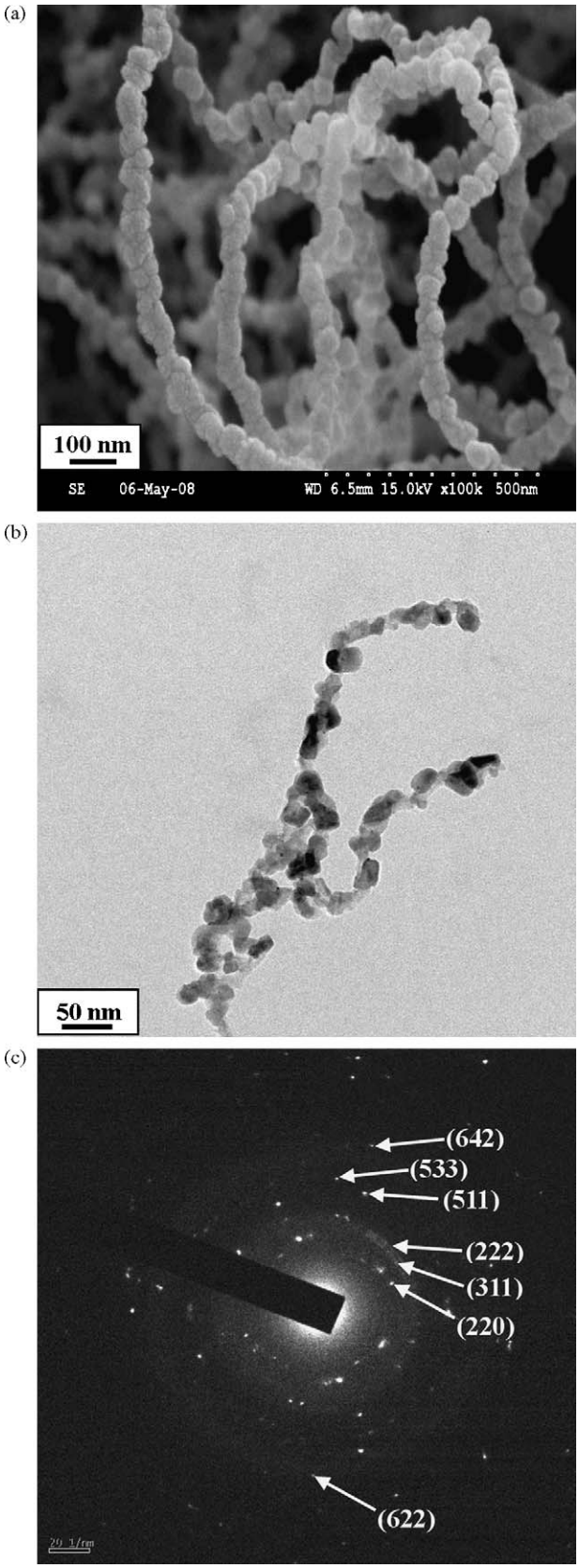

Fig. 4. (a) SEM image of SiO_x-core/Co-shell nanowires annealed at 500 °C. (b) TEM image of annealed SiO_x-core/Co-shell nanowires. (c) Associated SAED pattern.

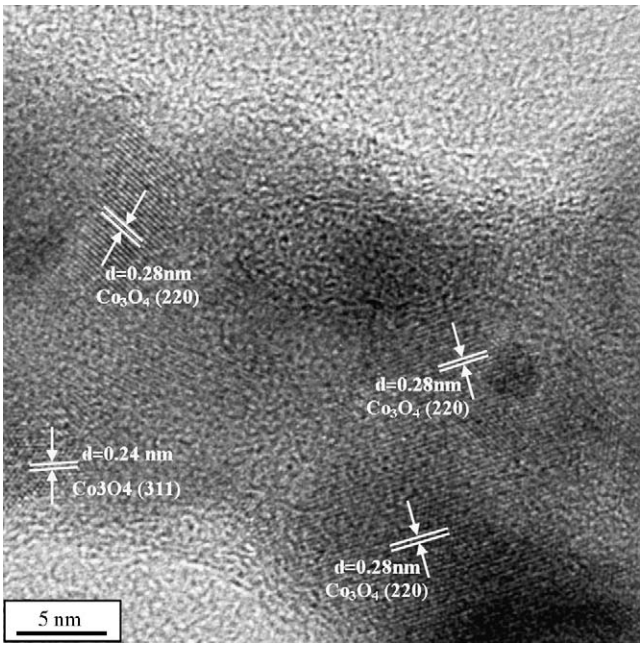

Fig. 5. Enlarged TEM image of an SiO_x-core/Co-shell nanowire annealed at 500 °C.

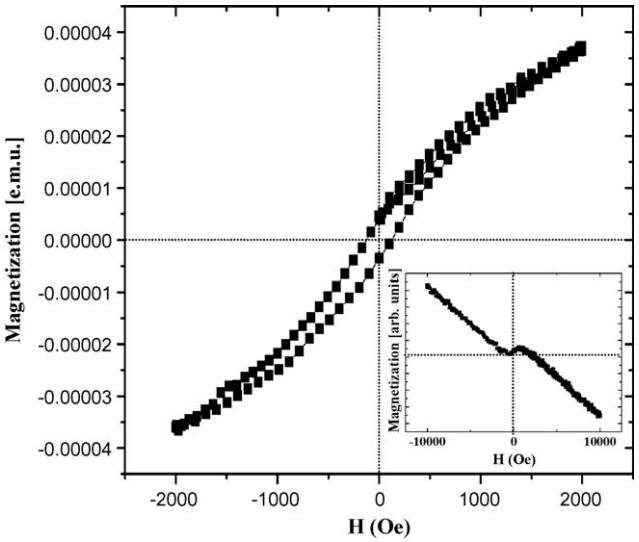

Fig. 7. Field dependence of magnetization curve for as-synthesized SiO_x-core/Co-shell nanowires (inset: field dependence of magnetization for SiO_x-core/Co-shell nanowires annealed at 500 °C).

In order to study the magnetic properties of the nanowires, we measured the field dependence of the magnetization (*M–H* curve) of the as-synthesized samples at room temperature. The hysteresis loop of the as-synthesized SiO_x-core/Co-shell nanowires is shown in Fig. 7. Although the hysteresis loop is not as clear as that of epitaxial Co nanowires [33], probably due to the nano-size Co grains embedded in the amorphous Co, the existence of coercivity (~128 Oe) and remnant magnetization (~4.15×10^{-6} emu) suggests that our SiO_x-core/Co-shell structures should have ferromagnetic properties. In addition, we noticed that the *M–H* curve is not well-saturated at large applied magnetic fields. Based on recent systematic studies of Co/CoO core/shell nanoparticles [34], we conjectured that some proportion of antiferromagnetic CoO might coexist in our SiO_x-core/Co-shell nanowires. On the other hand, the inset of Fig. 7 shows the *M–H* curve of samples annealed at 500 °C, which exhibits diamagnetic behavior presumably originating from the SiO_x core nanowires. We surmise that the disappearance of the ferromagnetic behavior upon thermal annealing is due to the transformation of Co into antiferromagnetic Co_3O_4.

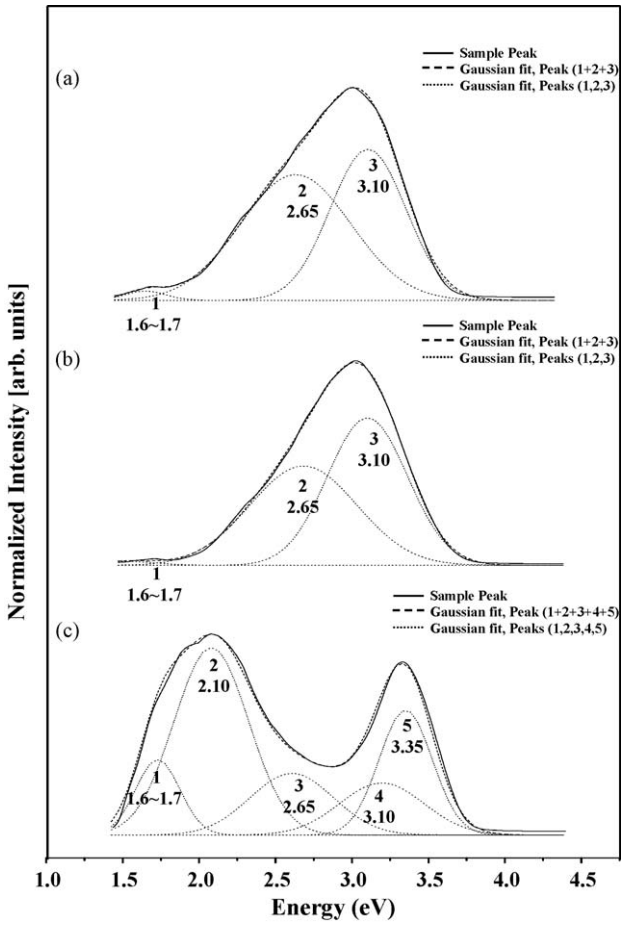

Fig. 6. Multi-peak fitted PL spectra of (a) core SiO_x nanowires prior to Co coating, (b) Co-coated SiO_x nanowires prior to thermal annealing and (c) Co-coated SiO_x nanowires which were annealed at 500 °C.

4. Conclusions

In summary, SiO_x-core/Co-shell nanowires were fabricated and the effects of thermal annealing on their properties were investigated. The SEM images reveal that the SiO_x-core/Co-shell nanowires have a 1D morphology with a smooth surface, whereas thermal annealing induced the formation of a rough surface. The XRD and SAED patterns and enlarged TEM images indicate that the sputtered nanowires comprise a cubic Co phase. Also, it was found that subsequent thermal annealing induced the formation of crystalline Co_3O_4 nanoparticles on the core SiO_x nanowires. PL measurements revealed that the Co shell does not contribute to the PL emission, whereas the Co_3O_4 structures added yellow and UV peaks. By measuring the field dependence of the magnetization, we observed that the SiO_x-core/Co-shell nanowires possess a slight hysteresis.

Acknowledgements

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