World Journal of Nano Science and Engineering, 2014, 4, 1-6
Published Online March 2014 in SciRes. http://www.scirp.org/journal/wjnse
http://dx.doi.org/10.4236/wjnse.2014.41001

Scientific Research

Role of Chromium Intermediate Thin-Film on the Growth of Silicon Oxide (SiO_x) Nanowires

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Received 27 December 2013; revised 28 January 2014; accepted 8 February 2014

Abstract

In the present work, one-dimensional nanostructures of silicon oxide (SiO_x) have been synthesized by thermal annealing method with and without chromium thin film on silicon substrate. The synthesis was carried out at different process temperatures ranging from 1000˚C to 1100˚C by using gold/chromium (Au/Cr) catalysts stack layer on the Si substrate in nitrogen (N_2) ambience. The as-synthesized SiO_x nanostructures have tetragonal rutile structure and show polycrystalline nature. The SEM images reveal wire-like nanostructures on the substrate with and without chromium thin film. Under the catalytic reaction of the gold/chromium metal, the density of SiO_x nanowires is enhanced, since the Cr layer serves as a diffusion barrier for the diffusion of the gold downwards into the Si substrate. The vapor-liquid solid (VLS) growth mechanism is found to be dominant in the growth of SiO_x nanowires. Furthermore, X-Ray diffraction microscopy (XRD) and Photoluminescence spectroscopy (PL) analysis conclude the defect free growth of the SiO_x nanowires on gold/chrome/silicon substrate.

Keywords

SiO_x Nanowires; Catalyst Assisted Growth; Gold; Chromium; Thermal Annealing

1. Introduction

Amorphous silicon oxide (SiO_x) nanowires have many potential applications in blue light emitters, optical sensors [1] and reinforcing composites [2]. These nanowires are generally grown with transition metal catalysts

How to cite this paper: Johari, A., Johari, A., Rana, V. and Bhatnagar, M.C. (2014) Role of Chromium Intermediate Thin-Film on the Growth of Silicon Oxide (SiO_x) Nanowires. *World Journal of Nano Science and Engineering*, **4**, 1-6.
http://dx.doi.org/10.4236/wjnse.2014.41001

(gold, iron, palladium etc.) at an elevated temperature. Liu *et al*. used Fe as a catalyst for the growth of the SiO_x nanowires [3]. Jiang *et al*. produced the SiO_x nanowires by using iron-cobalt-nickel (Fe-Co-Ni) alloy nanoparticles as the catalyst and showed that they had a strong blue-green emission [4]. Zhang *et al*. displayed that the SiO_x nanowires cloud can be formed on tin balls by chemical vapor deposition via vapor-liquid-solid (VLS) process [5]. Wang *et al*. reported that the amorphous SiO_x nanowires could be grown on the Si substrate by using platinum (Pt) as a catalyst [6]. Lin *et al*. synthesized the amorphous SiO_x nanowires from silicon monoxide powder under super critically hydrothermal conditions [7]. Park *et al*. used gold (Au) and palladium-gold (Pd-Au) thin film as the catalyst for the growth of amorphous SiO_x nanowires. These nanowires were grown via Solid-Liquid-Solid (SLS) mechanism [8]. However, thermal annealing is the simplest method for the growth of SiO_x nanowires. During the thermal annealing, a thin layer of the gold on the Si substrate is heated at growth of the high temperature (~1100˚C) in the presence of inert gas environment. At this temperature, some amount of the gold diffuses into the Si substrate. This reduced the density of the catalyst nanoparticles on the Si surface and resulted into a lower density of the nanowires. To enhance the density of nanowires, the diffusion of the gold into the Si substrate must be retarded. The gold diffusion can be retarded either by reducing the growth temperature or by inserting a barrier layer in the Au/Si catalyst system.

In present work, we have synthesized SiO_x nanostructures by thermal evaporation method with and without chromium thin film as a catalyst on Si substrate. During the growth of SiO_x nanowires, the diffusion of the gold into the Si substrate is retarded by inserting a thin layer of chromium (Cr) metal in the Au/Si substrate. The growth of nanowires was carried out with the gold/chromium/silicon (Au/Cr/Si) substrate at different temperatures ranging from 1000˚C to 1100˚C. To investigate the effect of the Cr layer, the nanowire growth was also carried out in the Cr/Si sample at 1100˚C and 1150˚C.

The as-synthesized products were analyzed with Scanning Electron Microscopy (SEM), X-Ray diffraction microscopy (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Transmission Electron Microscopy (TEM) and Photoluminescence spectroscopy (PL) for observing the effect of chromium thin film on the structural morphology, crystal structure, composition and optical properties of silicon oxide (SiO_x) nanostructures.

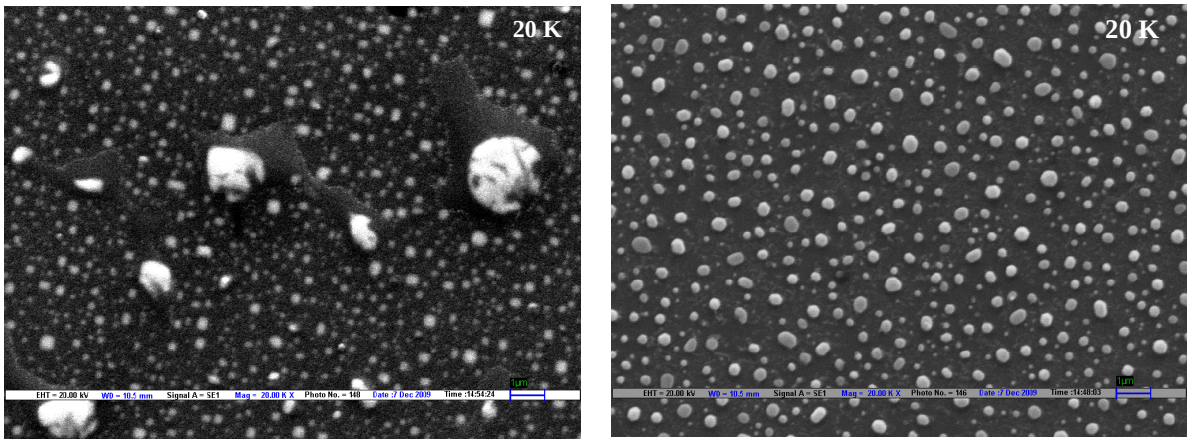
2. Experiments Details

N-type (100) Si wafer was used as a substrate for the growth of SiO_x nanowires. Before depositing the catalyst films of Au and Cr, the Si substrate was atomically cleaned by using Isopropyl alcohol (IPA) with ultrasonic vibrations, a mixture solution of H_2SO_4 and H_2O_2, and 10% HF solution for removing the native SiO_2. The gold (Au) and chromium (Cr) thin films were deposited on the Si surface in radio-frequency (RF) sputtering chamber at the pressure of 1×10^{-6} mbar and 100 watt power. The as-deposited thin layer of the Au and the Cr acts as catalyst for the growth of SiO_x nanowires. Two types of samples were fabricated which consists of Au/Si and Au/Cr/Si substrates. Successively, these samples were loaded into the maximum temperature zone of horizontal tubular furnace. The furnace temperature was maintained at various temperatures ranging from 1000˚C to 1100˚C. The nanowires were grown by thermal annealing of Au (20 nm)/Si and the Au (10 nm)/Cr (10 nm)/Si substrates in nitrogen (N_2) ambience. The synthesis was carried out at atmospheric pressure. The as-synthesized products were characterized by Scanning Electron Microscopy (SEM), X-Ray diffraction microscopy (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Transmission Electron Microscope (TEM) and photoluminescence spectroscopy (PL) for observing the effect of chromium thin film on the structural morphology, crystal structure and composition and optical properties.

3. Results and Discussion

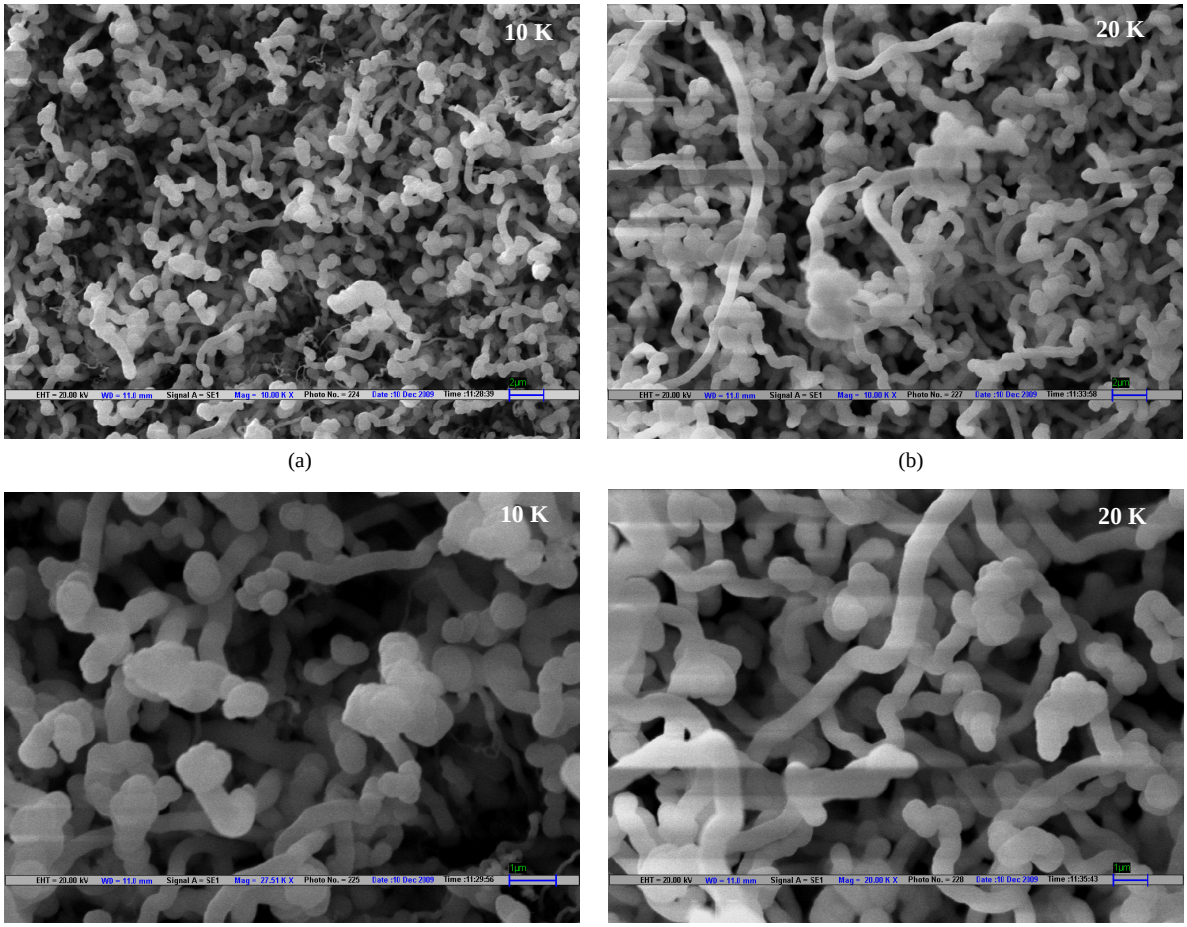
Figure 1 shows the typical SEM images of the Au (20 nm)/Si and Au (10 nm)/Cr (10 nm)/Si substrates annealed at 1000˚C for 40 min in N_2 ambience. Under these conditions, there was no evidence of the nanowire growth. However, the Au catalyst layer on both substrates is agglomerated into nanoparticles after the thermal annealing. The density of nanoparticles is higher in the Au (10 nm)/Cr (10 nm)/Si as compared to the Au (20 nm)/Si substrate. These nanoparticles serve as nucleation sites for the growth of nanowires. To initiate the growth of nanowire, process temperature is further increased to 1100˚C.

Figure 2 shows SEM images of the Au (20 nm)/Si and the Au (10 nm)/Cr (10 nm)/Si substrates annealed at 1100˚C for 40 min in N_2 ambience. At this temperature, both substrates show the growth of nanowires. However, the nanowires are homogeneously deposited over large area on the Au/Cr/Si substrate. This is due to the



(a) (b)

Figure 1. SEM images of the SiO_x nanowires synthesized at 1000˚C on: (a) Au/Si, (b) Au/Cr/Si sample.



(a) (b)

(c) (d)

Figure 2. SEM images of the SiO_x nanowires synthesized at 1100˚C on: (a) and (b) Au/Si, (c) and(d) Au/Cr/Si sample.

formation of higher density of the Au nanoparticles on the Au/Cr/Si substrate. The typical length of the SiO_x nanowires is several tens of micrometers while the width is in the nanometer range.

Further, to investigate the role of the Cr layer, the Si substrate with 10 nm thick Cr layer were annealed in N_2 ambience at 1100˚C and 1150˚C for 40 min. At these temperatures, the Cr thin film agglomerates into nanopar-

ticles on Si substrate but the samples do not show any sign of the nanowire growth. Thus, it can be concluded that the Cr layer does not act as a catalyst and only the Au metal layer serves as catalyst in the growth of nanowires.

The XRD pattern (**Figure 3**) reveals the overall crystal structure and phase purity of the as-synthesized products on Au/Si and Au/Cr/Si substrates annealed at 1100˚C for 40 min in the N_2 ambience. Most of the diffraction peaks can be indexed to the orthorhombic structure of SiO_2. No characteristic peaks of impurities, such as other oxides, were observed. The strong and sharp reflection peaks suggest that the well-crystallized SiO_x products were successfully obtained through the present synthesis method. Using Scherrer's formula, the average crystallite size was found to be about 300 nm.

Figure 4 shows HRTEM (**Figure 4 (a)**) and EDX spectra (**Figure 4 (b)**) of the as-synthesized products on Au (10 nm)/Cr (10 nm)/Si substrate annealed at 1100˚C for 40 min in N_2 ambience. The nanowire diameter was estimated in the range of 300 nm. The associated EDX analysis confirms that the synthesized products are composed of only Si and oxygen and no metal (Au and Cr) traces were observed in the nanowire. However, these metal nanopaticles may be present on the tip of the nanowire. This confirms that these metals only catalyze the growth of nanowires. The C and Cu related signals are due to the contamination of C while preparing HRTEM specimens and due to the presence of Cu grids respectively.

Figure 5 shows room temperature PL spectra of the SiO_x nanowires grown on the Au (20 nm)/Si and the Au (10 nm)/Cr (10 nm)/Si substrate at 1100˚C. Both samples show a sharp strong ultraviolet (UV) near band edge emission at 380 nm and Au (20 nm)/Si substrate exhibit emissions at 400 nm and 440 nm also. The emission at 400 nm is due to intrinsic diamagnetic defect centers [8] whereas Photoluminescence emission peaks at 380 nm and 440 nm is due to the oxygen deficiency [9] in the growth of nanowires. These results were also confirmed by the XRD which shows very high intensity peaks on the Au/Cr/Si substrate in comparison with the Au/Si substrate.

From above experiments, the nanowires growth mechanism is concluded in the following way: For the Au/Si as well as Au/Cr/Si substrate, no nanowires growth was observed at process temperatures of 1000˚C, shown in **Figure 1**. The nanowire growth was only observed at the elevated temperature of 1100˚C as shown in **Figure 2**. A higher density of nanowire was observed for the Au/Cr/Si catalyst than the Au/Si catalyst system. This phenomenon can be understood in a way that the Cr layer acts as a diffusion barrier for the Au and stops the inward diffusion of the Au into the Si and causes the higher density of the Au nanoparticles, which catalyze the nanowire growth. This results the higher density of the SiO_x nanowires on Au/Cr/Si substrate in comparison with the Au/Si substrate.

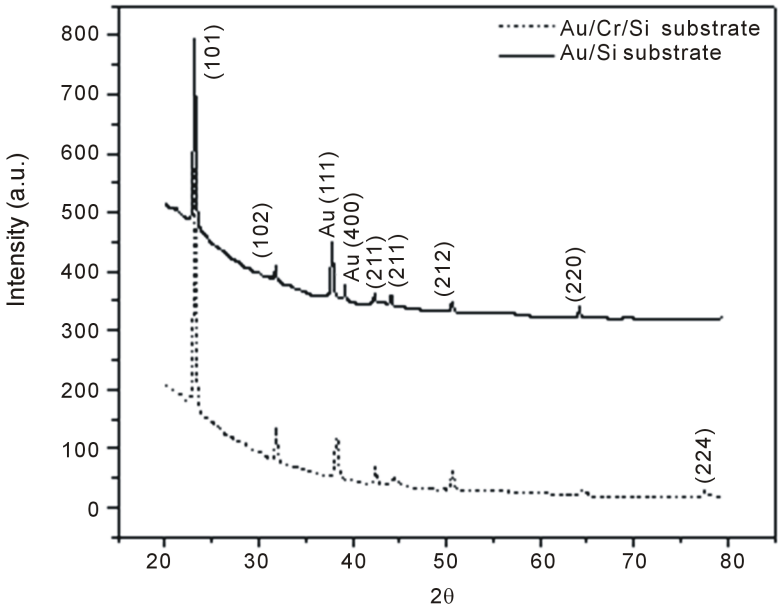
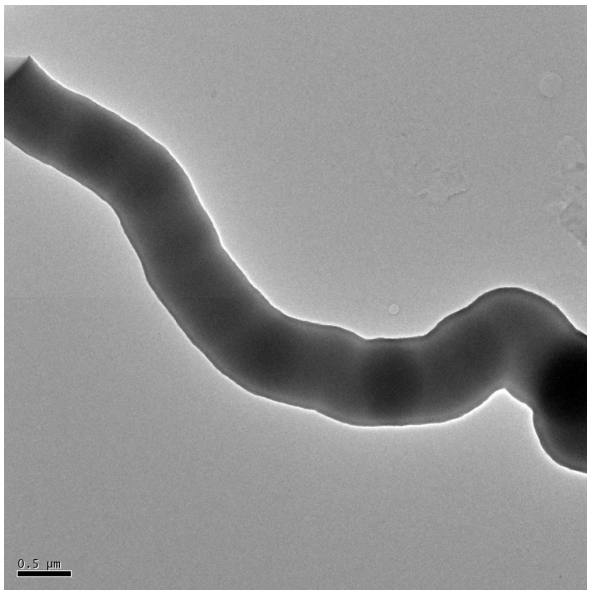
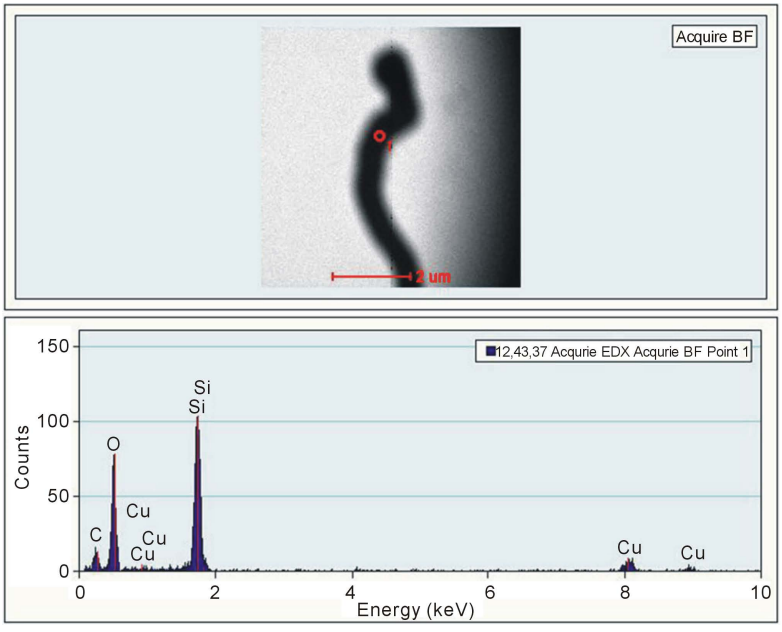


Figure 3. XRD image of the SiO_x nanowires synthesized at 1100˚C in N_2 ambience.



(a)



(b)

Figure 4. (a) HRTEM and (b) EDX images of the SiO_x nanowires synthesized at 1100˚C on the Au/Cr/Si sample.

In this growth process, the Au film agglomerates into the nanoparticles at relatively lower temperature than the Cr layer. This is due to the lower melting point of the Au film (melting point ≈ 1064˚C) in comparison to the Cr film (melting point ≈ 1857˚C) [4] [10]. Afterwards, the Si atom diffuses outward through the boundary between Cr particles and colloids with Au particles, the SiO_x nanowires are then formed due to super-saturation of the Si in the Au nanoparticles and their reaction with the ambience oxygen. Therefore, the Au layer is only responsible for the nanowire growth and the Cr layer serves only as a diffusion barrier.

4. Conclusion

We have synthesized the silicon oxide (SiO_x) nanowires on gold coated and gold/chrome coated Si substrate by

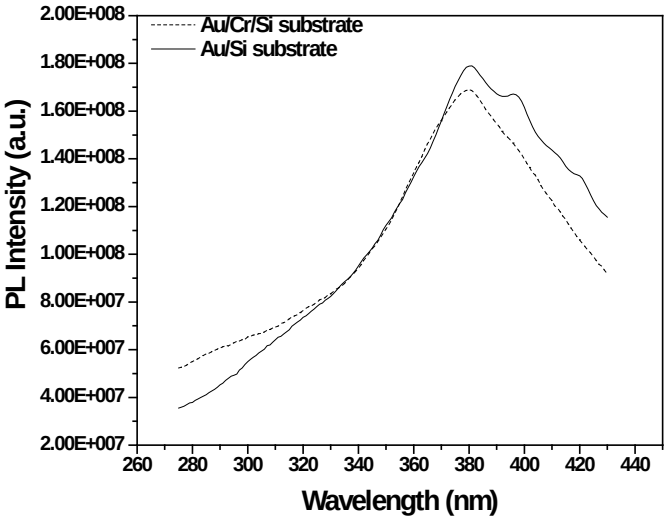


Figure 5. Room Temperature Photoluminescence spectra of the SiO_x nanowires.

thermal annealing process. The higher density of the SiO_x nanowires is attained at process temperature of 1100˚C by using the thin layer of the Cr metal on the Au/Si substrate. This is due to the fact that the Cr layers stop the inward diffusion of the Au into the Si and cause the higher density of the Au nanoparticles which catalyze the nanowire growth. The surface morphology study concludes the growth of nanowires. The synthesized nanostructures have orthorhombic structure and polycrystalline in nature. In the PL spectra of SiO_x nanowires, we have not observed any peak corresponding to oxygen deficiency on the Au/Cr/Si substrate whereas oxygen deficiency peaks exist on the Au/Si substrate. This confirms that we have synthesized defect free silicon oxide (SiO_x) nanowires by using chromium as an intermediate layer.

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