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Synthesis of In$_2$O$_3$ nanocrystal chains and annealing effect on their optical properties

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The authors reported the synthesis of indium oxide nanocrystal chains on silicon substrates using gold nanoparticles as catalyst on native silicon dioxide. Scanning electron microscopy investigations showed that In$_2$O$_3$ nanocrystal chains were formed. The nanocrystal chains comprised many well shaped octahedron nanoparticles with their size ranging from 20 to 100 nm connected with each other to form a network. Both high resolution transmission electron microscopy and diffraction pattern revealed that the In$_2$O$_3$ nanocrystal chains were single crystalline grown along the [111] direction. Photoluminescence study of In$_2$O$_3$ nanocrystal chains exhibited main photoemission at 544 nm due to the recombination between electrons in localized state induced by oxygen vacancies and holes in valence band. After the annealing treatment, the main photoluminescence peak not only slightly redshifted to 558 nm but also became narrower, which was attributed to the total localized state away from the conduction band caused by less defect distribution. © 2007 American Vacuum Society. [DOI: 10.1116/1.2710244]

I. INTRODUCTION

Indium oxide (In$_2$O$_3$) is a very important wide band gap of around 3.5 eV semiconductors and has recently attracted much interest as a material for transparent electrodes in electronic devices such as liquid crystal displays, solar cells, sensing material, and nanowire technology. In recent years, there has been increasing interest in the fabrication of In$_2$O$_3$ nanostructure because of their advantages to the understanding of novel physical properties and potential applications in nanoelectronic and optoelectronic devices. Kong and Wang obtained In$_2$O$_3$ nanobelts by evaporation of In$_2$O$_3$ powders. Li et al. grew In$_2$O$_3$ nanowires by a thermal evaporation oxidation method with a catalyst by laser ablation. Alina Magdas et al. grew In$_2$O$_3$ nanoarrows in thermally treated indium nitride for different times. Lao et al. observed nanochains and nanowire networks grown by a vapor transport and condensation method. Though many kinds of nanostructure of In$_2$O$_3$ were developed, the reports related to nanochain structure of In$_2$O$_3$ are still limited substantially.

In this article, we successfully synthesized In$_2$O$_3$ nanochains on silicon substrates using gold nanoparticles as catalyst on native silicon dioxide. The growth mechanism will be discussed in the following section. The structural and optical properties of In$_2$O$_3$ nanochains were analyzed in detail by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), x-ray diffraction (XRD), and photoluminescence (PL). The method of thermal annealing was also used. We investigated the effect of thermal annealing on optical properties of In$_2$O$_3$ nanochains and described the reasonable mechanism in photon emission.

II. EXPERIMENTS

Single crystal (001) oriented silicon wafers were used as substrates. Gold nanoparticles having diameters of ~20 nm were used as catalysts; they were produced by the chemical reduction of gold chloride tetrahydrate (HAuCl$_4$) with sodium citrate, and then spread onto a silicon wafer coated with a native oxide layer using a self-assembled monolayer of 3-aminopropyltrimethoxysilane as an adhesion agent. A two-zone vacuum furnace was used to grow the nanochains. Oxygen was the carry gas and flowed through the system at rate of 30 SCCM (SCCM denotes cubic centimeter per minute at STP). During the growth process, 2 g indium powders were positioned at the upstream with the samples placed at the downstream. The source vapor was transported by the carrier gas and condensed on the substrates. The temperatures were heated to 900 °C for sources and 700 °C for samples. The typical reaction time was 6 h and the growth pressure was around 0.1 torr. The morphology and microstructure of the samples were investigated by scanning electron microscopy (JEOL, JSM 6500F) and high resolution transmission electron microscopy (JEOL, JEM 2010F, operating at 200 kV). The compositions were analyzed using energy dispersive spectrometry (EDS) attached to the SEM. Selected area electronic diffraction confirmed crystal orientation of In$_2$O$_3$ nanochains. Afterward, the samples were furnace annealed in the temperature of 700 °C for 2 h in oxygen ambient. The crystal structure analysis was performed by the XRD measurement with Cu $K\alpha$ radiation. PL spectra were measured at room temperature by means of TRIAX-320 spectrometer using a 25 mW He–Cd laser with the emission wavelength of 325 nm as the excitation source.

III. RESULTS AND DISCUSSION

In general, for one-dimensional nanostructure growth, many researches have shown that the synthesis using vapor-
reacted with leakage oxygen near the original In$_2$O$_3$ particles to start nanochain growth. Once the latter indium vapor the gold catalysts nucleated with the adjacent In$_2$O$_3$ nanoparticles and gold catalyst played very important roles. We suggested the gold may still remain on the substrate surface, which means the indium vapor from the upstream formed alloy with several gold nanoparticles. Based on our experiment results, we found that the gold catalyst is necessary for the synthesis of the networks. However, we also observed many gold nanoparticles distributed on the substrate surface, which means the indium vapor from the upstream formed alloy with several gold nanoparticles. Meanwhile, there were also many aggregative octahedral In$_2$O$_3$ nanoparticles randomly dispersed on the substrate surface. In our growth process, therefore, the VS mechanism and gold catalyst played very important roles. We suggested it was likely that small octahedral In$_2$O$_3$ nanoparticles were formed in air and fell on the substrate at first. Consequently, the gold catalysts nucleated with the adjacent In$_2$O$_3$ nanoparticles to start nanochain growth. Once the latter indium vapor reacted with leakage oxygen near the original In$_2$O$_3$ nanoparticles/nanochains, there were more opportunities to form sequence of In$_2$O$_3$ nanoparticles and then synthesized long nanochains. We focused on different positions of In$_2$O$_3$ nanochains to proceed EDS measurement. The EDS spectrum, shown in the Fig. 1(c), indicates that the nanochains were essentially composed of indium and oxygen. The silicon peak came from silicon substrate and no gold was detected so that we suggested the gold may still remain on the substrate. Lao et al. grew In$_2$O$_3$ nanocrystal chains of similar shape as ours by using gold catalyst; meanwhile, they also found that there was not any gold within their nanochain structure.\(^8\)

Figure 2(a) shows the selected TEM bright-field image of In$_2$O$_3$ nanochains. The sizes of every particle in chains were different but the shapes were uniquely octahedral shape. The junction boundary can be clearly seen between the two nanoparticles. Figure 2(b) shows the high resolution TEM image of one nanoparticle. The corresponding selected area electron diffraction (SAED) is shown in Fig. 2(c), which proved our In$_2$O$_3$ nanoparticle with chains was a single crystal structure of excellent quality. Analysis of both TEM images and SAED revealed that the In$_2$O$_3$ nanochains are single crystalline and grow along the [111] direction.

We would further study the effect of thermal annealing with oxygen at 700 °C on the structure and optical characteristics of the In$_2$O$_3$ nanochains. The XRD patterns of the In$_2$O$_3$ nanochains treated with and without thermal annealing procedures are shown in Fig. 3. The patterns correspond to In$_2$O$_3$ with the cubic structure with lattice constant of a = 1.011 nm (Ref. 13). Both the XRD results revealed no additional peaks corresponding to metallic indium or gold since no indium precipitates and it is difficult to detect gold monolayer. We could see the same peaks occur in both samples, which indicated the thermal annealing for the crystal orientation of the sample could not cause obvious change. The strong intensities relative to the background signal also indicated high crystallization quality of the In$_2$O$_3$ nanochains. We measured the XRD (111) rocking curves in order to compare the quality between both samples. The comparison is shown in Fig. 4. The XRD line becomes stronger and narrower as the samples are treated with thermal annealing. However, there was no clear difference in morphologies of both samples. The annealing effect could generally facilitate

![Image](image-url)

**Fig. 1.** ([a] and [b]) Selected area SEM images of In$_2$O$_3$ nanochains grown on a Si substrate. (c) EDS results of In$_2$O$_3$ nanochains.

**Fig. 2.** (a) TEM bright-field image part of a nanochain. (b) HRTEM image of the nanochain. (c) The corresponding selected area electron diffraction pattern.
ion activation and repair defects. In other words, most defects will be pruned and the quality will be improved after annealing. Most of oxide semiconductors are native $n$-type material due to oxide vacancies. Therefore, we suggested that more oxygen atoms were filled into positions of vacancies when using oxygen as carrier gas during annealing progress.

The optical properties of In$_2$O$_3$ nanochains were investigated by PL measurement. The influence of thermal annealing on optical characteristics of In$_2$O$_3$ nanochains is shown in Fig. 5. Both PL intensity curves were normalized. After thermal annealing treatment, not only the PL peaks of In$_2$O$_3$ nanochains redshifted from 544 to 558 nm but the full width of half maximal of PL spectrum also became narrower. In addition, the integrated intensity of PL emission decreased abruptly after annealing. Moreover, there was another peak occurred at 357 nm after annealing. Since In$_2$O$_3$ is a semiconductor with a band gap of around 3.6 eV, our 544 and 558 nm PL emissions would not come from the transition of excitons from the conduction band to the valence band of In$_2$O$_3$ nanochains. On the other hand, the PL peak of 357 nm might originate from the radiative recombination of an excited carrier from the exciton state to the valence state. Many groups have studied on the optical properties of In$_2$O$_3$ compound and they have obtained different results. Liang et al. observed PL peaks at 470 nm from In$_2$O$_3$ nanofibers. Li et al. measured PL of the In$_2$O$_3$ nanotubes that exhibited emission of 593 nm. Lee et al. observed PL peak at 637 nm from In$_2$O$_3$ films. The above PL mechanism was mainly attributed to the effect of the oxygen deficiencies. The reason for electronic $n$-type property of In$_2$O$_3$ is that no sufficient oxygen atoms to catch electrons released from indium atom make these electrons form the donor level. The more free electrons exist in crystal, the smaller energy gap would be between conduction band and donor level. Therefore, both the PL peaks of 544 and 558 nm in our results not only revealed they were part of deep-level emission assigned to be defect-state-induced emission in In$_2$O$_3$ crystals but also indicated lower defect density caused redshift after thermal annealing, which was consistent with the results of XRD.

A schematic diagram of relative states is shown in Fig. 6. The $E_L$ represents main localized state. The oxygen vacan-
cies caused many localized states between the conduction and the valence band. The induced residual electrons in localized states would decrease after thermal annealing and exhibit a narrower linewidth in the PL spectrum. Meanwhile, the decreased numbers of electrons in the localized state produced redshift of PL peak. An electron could be excited to the upper energy level than main localized states by a pumping source and further to form an exciton. However, for oxide semiconductor materials, most native electrons from oxide deficiencies would recombine with the holes in the valence band, making the exciton emission less remarkable. Therefore, once fewer electrons were in localized states after thermal annealing in our case, there could be a higher opportunity of recombination between the upper level and the valence band for the emission peak of 357 nm. As to either this energy level is an exciton state or general defect level state, further experiments still shall be done to clarify it.

IV. CONCLUSION

In conclusion, we reported the synthesis of In$_2$O$_3$ nanocrystal chains on silicon substrates using gold nanoparticles as catalyst on native silicon dioxide. The nanocrystal chains comprised many well shaped octahedron nanoparticles with their size ranging from 20 to 100 nm connected with each other to form a network. We have discussed the growth mechanism and found crystalline grown along the [111] direction by analysis of TEM. PL study pointed out main photomission at 544 nm due to the recombination between electrons in the localized state induced by oxygen vacancies and holes in the valence band. After annealing treatment, the reduction of oxygen vacancies pushing the donor level away from the conduction band could make the main emission peak not only redshift to 558 nm but also show a narrower linewidth. Such self-assembled nanocrystal chains should have great potential for applications of novel optoelectronic devices and nanophotonics.

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