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A novel method to dope silicon nanowires with Er ions

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A novel method was applied to grow silicon nanowires (Si-NWs) doped with Er ions. At first the gold nanoparticles were sputtered to clean Si (100) surfaces, they were then coated with Si or Al source sol-gel solutions. Finally, the Si-NWs grew by a vapor-liquid-solid (VLS) mechanism, at the same time, the coating layers were sintered to oxide layers. This method was easy and lessened energy consumes. The oxide-doping layer was so thin that our eyes cannot observe it.

Key words: Er ion, Silicon nanowires, VLS mechanism, Sol-gel.

Introduction

Recently, much progress has been made with the Er doping of silicon-rich silicon oxide (SRSO), which consist of nanocluster Si embedded inside a SiO₂ matrix [1-8]. However, isolation of Si nanoclusters inside the SiO₂ matrix makes current injection into SRSO difficult, which raises questions about the realization of such devices. The newest research is focused on the doping of Si nanowires (Si-NWs), which have diameters in the range of 10-100 nm and with lengths exceeding 1 µm and, thus, provides a very high areal density of Er^{3+} ions in the case of Er-doping [9, 10]. For the application of Si-NWs, the traditional doping method is first to produce Si-NWs, then coat a sol-gel solution on the Si-NWs surface, and finally sinter. In this process, the coating thickness also has to be controlled to be as thin as possible for the sake of easy current injection into the oxide layer.

Moreover, Er^{3+} -doped Al₂O₃ planar waveguide films have been successfully prepared and the photoluminescence spectrum at 1.53 µm observed [11-15]. Al₂O₃ is an interesting matrix material used in planar waveguides, because not only does it have a relatively high refraction index (n = 1.64) waveguides clad with SiO₂ (n = 1.45) result in a high confinement of the optical mode in the waveguides, leading to efficient pumping and amplification [16], but also aluminum could be either a network former, supplying non-bridging oxygen bonds, or an octahedral-coordinated network modifier [17]. More importantly, aluminum is added to silica to improve its mechanical properties, low thermal expansion coefficients and high chemical durability [18-20]. In this paper, we apply a novel method to dope Si-NWs with Er ions. Firstly gold nanoparticles were sputtered on clean Si (100) surfaces, which were then coated with Si or Al source sol-gel solutions. Finally, the Si-NWs were grown by a VLS mechanism, at the same time, the coating layers were sintered to oxide layers. This process removes a calcination step, so the energy consume is reduced considerable. In addition, our results show that the oxide layer is so thin that it cannot be observed by naked eye, which is an advantage compared with the traditional method.

Experimental

ASB (Al(O-sec- C_4H_9)₃) and TEOS (Tetraethylorthosilicate) were used as oxide precursor compounds. The sol-gel solution was prepared in two steps [14]. TEOS was at first dissolved in ethanol and prehydrolized by the addition of water and hydrochloridric acid (TEOS/ EtOH/HCl/H₂O=1:10/0.01/2). This sol was divided into two. One was aged for 48h at room temperature for the Si source sol-gel; To the other, which was aged at room temperature for 24h, an ethanolic solution of ASB peptized with HCl (ASB/EtOH/HCl/H₂O=1:50: 0.1/2) was subsequently added to give a final Si/Al atomic ratio of 10:1 and was then aged for a further 48h at room temperature to become the Si-Al source sol-gel. In addition, half of the ethanolic solution of ASB peptized with HCl (ASB/EtOH/HCl/H₂O=1:50: 0.1/2) was also aged for 48 hr at room temperature as the Al source sol-gel. For the deposition of erbiumdoped coatings, ErCl₃·6H₂O was introduced in the aged TEOS and ASB solutions in the Er/Si and Er/Al atomic ratio of 0.18:1. A transparent, homogeneous and "baby pink" sol-gel solution was obtained for the next dip coating.

Gold nanoparticles were sputtered onto the $5 \times 10 \times 1$ mm³ Si (100) wafers to give a thickness of 2 nm. These

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wafers were dipped into the prepared sol-gel solution. The dip-coating process was controlled to-and-fro for three times at the rate of 100 mm/minute, then dried in an Ar flow.

Si-NWs were grown on the coating Si (100) wafers by the VLS mechanism in a quartz tube furnace. During growth, H₂ and Ar gases were introduced at a flow rate of 100 sccm, respectively. SiCl₄ was introduced using H₂ carrier gas that was bubbled through liquid SiCl₄ held at 5 °C at a flow rate of 5 sccm. The growth temperature was 800-900 °C. As a result, silicon wafers with grown Si-NWs were obtained.

The phase structure of the Er-doped SiO₂, Al₂O₃ and SiO₂-Al₂O₃ powders produced by the sol-gel method was examined using a Siemens D500 X-Ray Diffraction instrument with Cu K α (λ =0.15418 nm) radiation at a scanning rate of 5° per minute from 2 θ =10° to 2 θ =70°. Thermo gravimetric analysis (TGA, Perkin-Elmer, TGA6) was carried out in an air atmosphere. During the measurements, the sample was heated at a rate of 10 Kminute⁻¹ over a temperature range of 30-900 °C.

Results and Discussion

In order to select a temperature to fit both the sintered oxide and Si-NWs growth, a TGA experiment was executed. As shown in Figure 1, there is a large decrease in weight below 100 °C, and an obvious weight loss between 100 °C and 700 °C, furthermore a slow weight loss from 700 °C to 900 °C. This may be explained that the lost weight below 100 °C is the adsorbed water and the organic solvent. Between 100 °C and 700 °C it is mainly due to the polymerization of the hydroxyl groups which sinter to oxides at higher temperature up to 900 °C. From the former studies [21], when the temperature is higher than 900 °C, the crystallization of the oxide will increase, which is not a benefit to the requirement for optical applications, although more OH groups will be removed at the higher temperature. However, 900 °C is also the temperature where



Fig. 1. TGA curve of Er³⁺ doped Si-Al sol-gel.



Fig. 2. Powder XRD patterns of Er^{3+} doped Si and Al oxides sintered at 900 °C. Round (\bigcirc) represents Er_2O_3 peaks; Triangle (\triangle) represents SiO₂; Squares (\square) represents θ -Al₂O₃ peaks. (a) SiO₂ (b) Al₂O₃-SiO₂ (c) Al₂O₃.

Si-NWs grow. In order to dispose of most of the OH groups, we selected 900 °C as the experimental temperature.

Figure 2 shows the powder XRD patterns of Si, Al and Er^{3+} doped Si-Al oxides sintered at 900 °C. Figure 2(a) is the XRD pattern of the SiO₂ with a broad band from 2 θ =21° to 2 θ =34° related to the silicon oxide amorphous matrix [PDF 450131]. Figure 2(c) is the XRD pattern of the Al₂O₃. As shown in Fig. 2(c), the characteristic XRD pattern of θ -Al₂O₃ phase (PDF 110517) was observed, which is consistent with former reports [13, 15] that when the sintered temperature is at 900 °C, the γ -Al₂O₃ transfer to θ -Al₂O₃ phase. Moreover, the θ -Al₂O₃, SiO₂, and Er₂O₃ (PDF 431007) phases are all observed in Fig. 2(b).

In order to obtain silicon nanowires (Si-NWs) doped with erbium (Er) ions, different processes were applied to dope the Er ions by the sol-gel solutions. Firstly, aluminum and silicon source sol-gel solutions doped with Er ions were prepared. Then, different steps were implemented. The first, gold nanoparticles were sputtered on pieces of clean Si (100) wafer to create 2-nmthickness layers, and transferred to the different sol-gel solutions, then dried and put into a quartz furnace to grow nanowires.

Figure 3 shows the scanning electron microscope (SEM) images of as-grown Si-NWs doped with Er ions. Figure 3a and 3b show the images of Si-NWs, which grew from coating Si and Si-Al source sol-gel solutions on the gold layer. As shown in Fig. 3a and 3b, big cracks can be observed, and the Si-NWs grew in the crack spaces and at the bottom of the blocks. Sometimes, the nanowires will expand to the surface of the blocks. As shown in the zoom image, the Si-NWs are not uniform. Some are straight with thick or thin diameters; some are curving. As with the former studies [22], the substrate, Si wafer, will define the array of



Fig. 3. SEM images of Si-NWs doped with Er^{3+} derived sol-gel Si, Al and Si-Al materials. (a) Si source sol-gel (b) Si-Al source sol-gel (c) Al source sol-gel (d) zoomed image in (c).



Fig. 4. Schematic structure of gold particles dispersed on the Si (100) surface.

nanowires. Due to the extensive shrinkage of the solgel film coating on the gold layer, the gold particles perhaps clustered during the sintered process. As shown in Fig. 4b not Fig. 4a, the higher layers of gold nanoparticles will not be controlled by the Si (100) wafer. As a result, it is assumed that the morphology of the nanowires will be curved when the higher layer gold nanoparticles act as the catalyst. In other words, the size of the gold catalyst particle will control the diameter of Si-NWs [23], the difference of the gold particle size and the gold clusters perhaps lead to the different diameters of the Si-NWs. Energy-dispersive X-ray (EDX) analysis performed on trapped Si-NWs in Fig. 3a and 3b showed that only Si element without Er and Al elements exists in these nanowires. Perhaps this is due to the large crack and the blocks of the film, which prevents the nanowires growing from the oxide-layer.

Figure 3c and 3d are SEM images of Si-NWs grown from a coating Al source sol-gel solution on a gold layer for different times. As shown in Fig. 3c, the Si-NWs grew in a large area with small cracks. As shown



Fig. 5. EDX analysis of Si-NWs doped with Al and Er oxides.

in the zoom image, even in the region which is not continuous, the Si-NWs are linked, which will make current injection continuous. Former repots have proved that an Al source film possesses good mechanical properties with a small shrinkage of the film during the drying process [24, 25], which perhaps makes the gold particles disperse well. As a result, it is assumed that during the sintering process of the sol-gel film, more free room is availabel for the growth of Si-NWs. A detailed mechanism should arise from future research. As shown in Fig. 3d, the Si-NWs are uniform exceptin diameter, and are all straight, indicating that the gold particles dispersed well on the substrate of the Si (100) wafer. The different diameters of the Si-NWs perhaps are due to the different catalyst size of the original gold particles during sputtering. EDX analysis (Fig. 5) taken on the trapped Si-NWs in Fig. 3d shows that not only the Si element but also Er and Al elements exist in these nanowires, which proves that the Si-NWs are doped with Er. The Er/Al mole ratio (0.27) is similar to our original source. On the other hand, oxides cannot be observed obviously in Fig. 3d, which is very different from other methods by sol-gel coating. This method supplies a thinner oxide layer, which is of benefit to the electron transfer from Si-NWs to Er ions.

Conclusions

The sol-gel materials lost the absorbed water and organic solvent below $100 \,^{\circ}$ C. The polymerization of the hydroxyl groups and sintering to oxides occurred at higher temperatures up to $900 \,^{\circ}$ C.

A novel method to dope Si-NWs with Er ions was applied, which reduces a calcination step.

The substantial shrinkage of the Si and Si-Al source sol-gel film coatings on the gold layer led to Si-NWs, which only grew on the bottom of the cracks and blocks and without Er ion doping.

The Si-NWs grew over a large area with small cracks when the Si (100) wafer was coated by Al source solgel solution. Even in the discontinuous region, the Si-NWs were linked. Er and Al elements were also observed. In addition, our results show that the oxide layer is so thin that it is invisible to the naked eye, which is very different from the traditional method.

This simple method supplies a novel technology to dope a rare earth into Si-NWs, which perhaps improves the transfer efficiency of the current injection.

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