Sonochemical Coreduction Route to Single-Crystalline InSb Dendrites

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Single-crystalline InSb dendrites were prepared by a sonochemical coreduction route. The result of supplementary experiments shows the experiment was carried out along the coreduction mechanism. It is found that the ultrasonic power, reaction temperature and solvent played crucial roles in the crystallinity and yield of products.

The III–V compounds have been of interest for their electronic and optoelectronic properties. Among those compounds, InSb is a type of important semiconductor due to its small bandgap (0.17 ev) and largest carrier mobility at room temperature (7.8×10^4 $cm^2 \cdot V^{-1} \cdot s^{-1}$), and can be used in making high-speed transistors.[1–3]

Morphology of dendrites as a type of fractal has attracted much attention recently. Many methods have been used to synthesize the dendrites supramolecular nanostructures.[4,5] But most methods of preparation to dendrites structure were colloidal reactions.

Traditionally, InSb has been prepared by solid-state reaction,[3,6–8] metallo-organic vapor phase deposition,[9] dehalosilylation reactions,[10,11] and solvothermal reduction methods.[12] However, all these routes required toxic precursors or solvents, high reaction temperatures, and complicated instruments. In this letter, with glycol as the solvent, $InCl_3 \cdot 4H_2O$, $SbCl_3$, and Zn powder as the reactants, a sonochemical coreduction route was reported to prepare InSb dendrites. This process is described as follows.

$$InCl_3 + SbCl_3 + 3Zn \xrightarrow{\text{glycol}} InSb + 3ZnCl_2 \qquad (1)$$

$InCl_3 \cdot 4H_2O$ (1.470 g, 5 mmol), $SbCl_3$ (0.455 g, 2 mmol), and Zn powder (0.975 g, 15 mmol) were loaded into a 100-mL reactor that was then filled with glycol up to 90% of the total volume. The reactor was designed to ensure that the horn tip was immersed into the solution consistently to the same depth (10 mm). The sealed reactor was kept in a circulating water bath to maintain the temperature of the bulk solution at 25 ± 5 °C and was irradiated with a high-intensity ultrasonic probe (Model, 1.5-cm Ti horn, 20 kHz, 100 $W \cdot cm^{-2}$) for 4 h. The precipitate was filtered and washed several times with diluted HCl (1 $mol \cdot L^{-1}$), distilled water and absolute ethanol. The product was dried in a vacuum at 60 °C for 2 h.

Figure 1a shows the X-ray diffraction (XRD) pattern[13] of the products. All the peaks can be indexed as cubic InSb with lattice constant a = 6.474 Å, which agrees with the reported data. (JCPDS card, NO. 6-208, a = 6.4781 Å). No impurities, such as In or Sb, can be detected. Transmission electron microscopy (TEM) images[13] (Figures 2a and b) reveal that products are some dendrites. Electron diffraction (ED) pattern[13] (Figure 3a) shows the dendrites were single-crystalline InSb.

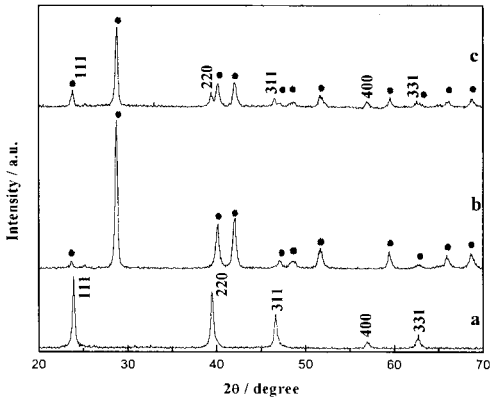


Figure 1. XRD patterns of the samples; circle = Sb; (a) products obtained at 25 °C, 100 $W \cdot cm^{-2}$; (b) products obtained at 0 °C, 6 $W \cdot cm^{-2}$; (c) products at 40 °C, 6 $W \cdot cm^{-2}$.

To investigate the reaction mechanism and the influence of ultrasonic power and reaction temperature on the crystallinity and yield of products, two experiments were carried out by the same route at 0 ± 5 °C or 40 ± 5 °C, which were kept in low-intensity ultrasonic reactor (6 $W \cdot cm^{-2}$). The as-prepared products were pure Sb (Figure 1b) and the mixture of Sb and InSb (Figure 1c), respectively. Moreover, it is found trace water in $InCl_3 \cdot 4H_2O$ was necessary for the formation of InSb. From these results, the mechanism is thought as follows.

$$H_2O \longrightarrow H\bullet + \bullet OH \qquad (2)$$

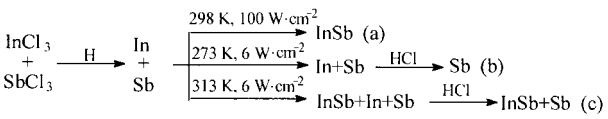
$$Zn + 2\ \bullet OH \longrightarrow Zn(OH)_2 \qquad (3)$$

$$InCl_3 + SbCl_3 + 6H\bullet \longrightarrow In + Sb + 6HCl \qquad (4)$$

$$3Zn(OH)_2 + 6HCl \longrightarrow 3ZnCl_2 + 6H_2O \qquad (5)$$

$$In + Sb \longrightarrow InSb \qquad (6)$$

The process of equation (6) needs relatively high ultrasonic power and reaction temperature, so the reaction was incomplete in above experiments. The produced In might be removed by the diluted HCl and the produced Sb could not be dissolved in the diluted acid. The whole process can be described as Scheme 1.



Scheme 1.

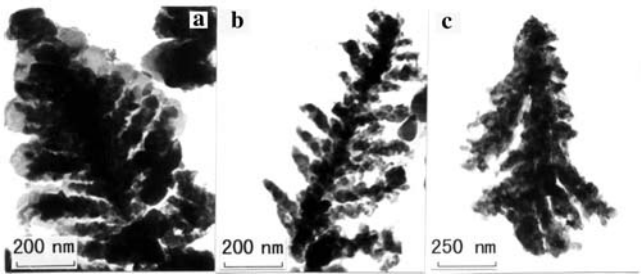


Figure 2. TEM images of the samples; (a), (b) products obtained at 25 °C, 100 W·cm^{-2}; (c) products obtained at 40 °C, 6 W·cm^{-2}.

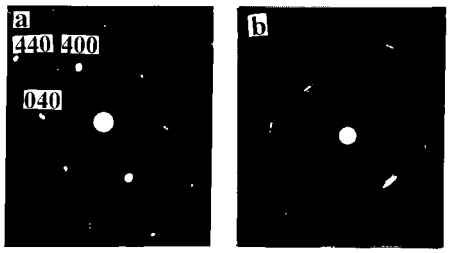


Figure 3. ED patterns of the samples; (a) products obtained at 25 °C, 100 W·cm^{-2}; (b) products obtained at 40 °C, 6 W·cm^{-2}.

The TEM image and ED pattern of the products prepared at 40 °C, 6 W·cm^{-2} are shown in Figure 2c and Figure 3b. It is found that the InSb in the products was dendrites with poor crystallinity. Moreover, the fractal morphologies were not very clear and the sizes were smaller than that of as-prepared products at 25 °C, 100 W·cm^{-2}.

It is also found that the solvent glycol played an important role in the formation of InSb. When ethylenediamine as solvent, the reaction system was alkalescent, which was not helpful to the reducibility of Zn powder. So some oxides impurities were obtained in the products. When ethanol or glycerol was used as solvent, the viscosity of reaction system was too low or too high, respectively. Too low viscosity was not helpful to the nucleation, while too high viscosity was not helpful to crystal growth. Therefore, glycol is optimum solvent for this reaction.

The cause of formation of dendrites is very complicated, and has been reported by many groups. Most scientists thought that the formation of dendrites is due to non-equilibrium growth and molecular anisotropy.[14,15] Based on their previous research, we think the formation of dendrites is related to the ultrasonic cavitate. The surge, growth, shrink and collapse of ultrasonic cavitate went with the diffusion of its local energy,[16] which brought out the non-equilibrium growth. On the other hand, produced In might be turned into liquid In flux under the ultrasonic energy. Thus the formation of InSb is anisotropic, which is helpful to the growth of dendrites.

In summary, a sonochemical coreduction route was reported to prepare the single-crystalline InSb dendrites. It is found that the reactions were carried out along the coreduction mechanism and the ultrasonic cavitate was crucial to the formation of dendrites. This technique is expected to prepare dendrites of other compounds.

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13 XRD patterns were carried out on a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromatized high-intensity Cu Kα radiation (λ = 1.54178 Å). The accelerating voltage was set at 50 kV, with 100 mA flux at a scanning rate of 0.06°/s in the 2θ range of 20° to 70°. The TEM images and ED patterns were taken on a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV.
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