NOTE

Low-temperature chemical synthesis of nanostructured indium nitride from indium hydroxide

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Nitridation of oxides is a conventional method to prepare nitrides. However, this method has a disadvantage of requiring a high reaction temperature. Additive-assisted nitridation is an effective route to synthesize nitrides at low temperature. In this study, hexagonal phase indium nitride (InN) nanomaterials have been successfully synthesized through the nitridation of indium hydroxide by sodium amide in a stainless-steel autoclave at a low temperature (250–300°C), in which sodium thiosulfate acts as an additive. Scanning electron microscope image shows that the as-obtained InN sample is composed of nanoparticles and nanosheets. The influences of the reaction temperature on the as-obtained product have also been investigated.

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Group IIIA nitrides (BN, AlN, GaN and InN) are important semiconductors for their excellent properties such as high chemical inertness, radiation resistance, and high thermal conductivity.^{1,2)} Among them, hexagonal phase indium nitride (InN) is a direct band-gap semiconductor with a narrow band-gap of about 0.70 eV, which has potential applications in photoelectronic devices.³⁾

Among group IIIA nitrides, the preparation and application of BN, AlN and GaN have been extensively studied. However, the decomposition temperature of InN is relatively low (about 500°C), which makes the preparation of InN more difficult.⁴⁾ Because of the most challenging in production of InN nanomaterials, their properties and applications have not been well-investigated. Up to now, considerable efforts have been made in synthesizing nanostructured InN through different synthetic methods such as pyrolysis of In(NH₂)₃,⁵⁾ organometallic precursor routes,⁶⁾ high-pressure direct synthesis,⁷⁾ and high-temperature ammonolysis.⁸⁾ Takai et al. have synthesized InN thin films by reactive magnetron sputtering.⁹⁾ InN thin films can also be obtained through a metalorganic vapor phase epitaxy.¹⁰⁾ InN single crystals have been prepared by UV-assisted atomic layer epitaxy.¹¹⁾ Plasma-assisted atomic layer deposition can also be used to synthesize vertical III-nitride cylinder arrays.¹²⁾ Solvothermal synthesis of InN nanocrystalline has been reported in superheated

toluene.¹³⁾ Xu et al. have synthesized InN nanowires and nanotubes by catalyst-free chemical vapor deposition at about 800°C.¹⁴⁾ InN nanowires with lengths of 30–50 μm have been synthesized by nitriding of indium sesquioxide at 680–720°C.¹⁵⁾ Hsieh and his co-workers have synthesized InN nanocrystals with a diameter of 6 nm from InBr₃ and NaNH₂ at low temperature.¹⁶⁾ InN crystals can be obtained from the reaction of LiInO₂ and NaNH₂ at 240°C.^{17,18)} However, it is still a challenging task to synthesize InN through one-step chemical reaction at low temperature from cheap and rich raw materials.

Recently, an additive-assisted route has been reported to synthesize borides, nitrides, and carbides at a relatively low temperature in our research group.^{19–25)} In this work, we report a new solid-state route to synthesize InN nanoparticles through a solid-state reaction of In(OH)₃, Na₂S₂O₃ and NaNH₂ at 250–300°C. The synthetic method in this paper has the advantages of simple and feasible, low cost, high yield, and low reaction temperature.

The chemical reagents were used in the experiment without further purification: Na₂S₂O₃ (Sinopharm Chemical Reagent Co., Ltd., >99%), In(OH)₃ (Shanghai Macklin Biochemical Co., Ltd., 99.99%), NaNH₂ (Sinopharm Chemical Reagent Co., Ltd., >98%), HCl (Chinasun Specialty Products Co., Ltd., analytical pure) and absolute ethyl alcohol (Sinopharm Chemical Reagent Co., Ltd., analytical pure). In a nitrogen-filled glovebox, In(OH)₃ (0.83 g), NaNH₂ (6.00 g), and Na₂S₂O₃ (1.58 g) were added into a stainless steel autoclave (about 22 mL capacity). Then, the autoclave was sealed tightly. The autoclave was heated to 300°C in a resistance furnace and maintained at

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300°C for 10 h. After cooling to room temperature, the autoclave was opened, and absolute ethyl alcohol was added in the autoclave. The black product was collected from the autoclave and washed with distilled water and diluted HCl. The product was dried in vacuum oven at 60°C for 10 h.

The as-obtained products were investigated by X-ray diffraction [XRD, Philips, Cu K α λ = 1.54178 Å (1 Å = 0.1 nm)], field emission scanning electron microscope (FE-SEM, JEOL-JSM-6700F), transmission electron microscopy (JEOL-2010), X-ray photoelectron spectrometer (XPS, ESCALAB 250 spectrometer), and Raman spectrometer (Invia Raman spectrometer with an excitation laser wavelength of 514.5 nm).

The crystal structure of the as-obtained product is determined from the XRD pattern (shown in Fig. 1). All the diffraction peaks in Fig. 1 can be indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), and (202) diffraction planes of the hexagonal phase InN, respectively. The lattice parameters a = 3.5382 Å, and c = 5.7037 Å have been extracted from the XRD pattern, which are close to the values of a = 3.5400 Å, and c = 5.7040 Å (InN, JCPDS card No. 65-3412). Debye–Scherrer formula can also be used to estimate the crystalline size of the as-obtained InN product. According to the Debye–Scherrer formula and the half-peak width of the InN (100) diffraction peak, the calculated size of the as-obtained InN product is about 48 nm.

The morphologies of the as-obtained InN product are investigated by SEM and transmission electron microscope (TEM). From the SEM image [Fig. 2(a)], we found that the as-obtained InN product is composed of nanoparticles and hexagonal nanoplates (indicated by arrows).

The TEM image [Fig. 2(b)] shows the average size of the InN nanoparticles is about 50 nm. Some fractured hexagonal InN nanoplates can also be found in the TEM image. A high-resolution TEM (HR-TEM) image of the as-obtained InN product is shown in Fig. 2(c). The regularly arranged lattice fringes have been found in Fig. 2(c), the distance is about 0.283 nm, which corresponds to the (002) plane spacing hexagonal InN. All the above results prove that InN with high crystallinity has been synthesized through our designed chemical reaction. The energy dispersive X-ray spectrometry (EDS) [shown in Fig. 2(d)] is employed for composition determination of the as-obtained InN product, which confirms that the as-obtained product consists of elements In and N. The Cu peaks in the EDS is come from the TEM grid.

Fig. 1. XRD pattern of the as-obtained product.

Fig. 2. FE-SEM image; (b) TEM image; (c) HR-TEM image of the InN product; (d) the corresponding EDS.

Fig. 3. XPS spectra of the InN product: (a) survey spectrum; (b) In3d region; (c) N1s region. (d) Raman spectrum of the as-obtained InN product.

Fig. 4. XRD patterns of the products without HCl treatment obtained at different reaction temperatures: (a) 200°C, (b) 250°C.

The composition of the as-obtained InN product is investigated by XPS spectra. A typical survey spectrum of the InN product is shown in **Fig. 3(a)**, which shows the product contains the elements In and N. The appearance of other peaks is due to the absorption of O_2 and CO_2 impurities on the surface of the product. The two peaks in **Fig. 3(b)** centered at 444.78 and 452.36 eV correspond to the $In3d_{5/2}$ and $In3d_{3/2}$ binding energies of InN, respectively. The peak in **Fig. 3(c)** centered at 396.10 eV corresponds to the N1s binding energy of InN. These results are close to the reported values for bulk InN.²⁶⁾ A typical Raman spectrum of the as-obtained InN product is shown in **Fig. 3(d)**. The three peaks centered at 486, 537, and 576 cm^{-1} correspond to the $E_g(TO)$ mode, $B_1(high)$ mode, and $A_1(LO)$ mode of InN, respectively. The Raman spectrum is consistent with the result of the reported work,¹⁷⁾ which

further proves that crystalline InN has been obtained through our synthetic route.

To investigate the effect of sodium thiosulfate in the formation process of InN, we found that InN cannot be obtained from the reaction of $NaNH_2$ and $In(OH)_3$ through a similar experimental process. Therefore, sodium thiosulfate is an essential ingredient in the formation process of InN. In order to study the effect of reaction temperature on the product, some relevant experiments are carried out. From the XRD pattern of the as-obtained product, element sulfur is found in the obtained product at the reaction temperature of 200°C [**Fig. 4(a)**], which may be decomposed from sodium thiosulfate. When the reaction temperature is 250°C, InN can also be obtained through this method [**Fig. 4(b)**], but the yield of InN is relatively low. The yield of InN can be improved by prolonging the

reaction time at 250°C. The yield of InN is about 80% (according to the quality of indium hydroxide) at the reaction temperature of 300°C for 10 h. In our synthetic experiments, neither expensive indium compounds nor a toxic ammonia flow is required. In addition, this synthesis method has the advantages of simple apparatus, low temperature, and high yield.

In summary, this work describes a novel thermal conversion route to InN nanomaterials from indium hydroxide. XRD pattern indicates that the product is hexagonal phase InN with the lattice parameters $a = 3.5382 \text{ \AA}$, and $c = 5.7037 \text{ \AA}$. Electron microscope images further reveal that the as-obtained InN product is composed of nanoparticles and hexagonal nanoplates. The influences of the reaction temperature on the as-obtained product have also been investigated. This simple method can also be applied to preparation of other metal nitrides.

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