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A mild reduction-phosphidation approach to nanocrystalline GaP

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Abstract

Nanocrystalline gallium phosphide (GaP) has been prepared through a reduction–phosphidation by using Ga, PCl₃ as gallium and phosphorus sources and metallic sodium as reductant at 350 °C. The XRD pattern can be indexed as cublic GaP with the lattice constant of a=5.446 Å. The TEM image shows particle-like polycrystals and flake-like single crystals. The PL spectrum exhibits one peak at 330 nm for the as-prepared nanocrystalline GaP. © 2004 Published by Elsevier Ltd.

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1. Introduction

Semiconductor nanoparticles are interesting materials because they have chemical and physical properties different from those of the corresponding bulk and isolated atoms or molecules [1–4]. Residing in the mesoscopic regime between the molecular and bulk regimes, semiconductor nanocrystals have unique electronic, magnetic and optical properties due to their small size and large surfaceto-volume ratio [5,6]. Recently, quantum size effects on the optical properties have been predicated to be more evident in the III–V group semiconductor nanomaterials than that in II–VI semiconductor nanomaterials [7]. Therefore, it is important to further study the synthesis and properties of III–V group semiconductor nanomaterials under mild conditions.

GaP is an indirect gap semiconductor and has many important applications in microelectronic devices. The most

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important way to prepare GaP is the metal-organic route. Dougall and co-workers [8] have reported that GaP semiconductor clusters can be synthesized in zeolite by using the reaction (Me₃)Ga and PH₃. At refluxing temperature, GaP nanocrystallines were obtained from GaCl₃ and P(SiMe₃)₃ or (Na/K)₃P and GaX₃ in toluene or other solvent, respectively [9,10]. Another important method for preparing GaP is the solid-state metathesis, in which GaX₃ (X=F, Cl, I) and Na₃P are used as the raw materials [11,12].

Herein, we provide a route to prepare nanocrystalline GaP at 350 °C by the reduction–phosphidation method, in which phosphorus trichloride (PCl₃) and gallium (Ga) are used as source materials and metallic sodium (Na) as the reductant. The reaction can be expressed as follows:

$$Ga + PCl_3 + 3Na \xrightarrow{350 \circ C} GaP + 3NaCl$$

2. Experimental procedure

All the manipulations were carried out in a dry glove box with Ar flowing. In the typical process, 0.01 mol Ga, 0.01 mol PCl₃ and 0.03 mol Na were placed into a stainless

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Fig. 1. XRD pattern of the GaP sample.

steel autoclave with a quartz liner. And then, the autoclave was sealed and heated at 350 °C for 6 h, followed by naturally cooling to room temperature. The product in the quartz liner was washed with distilled water and absolute

ethanol for several times to remove the impurities. The final product was vacuum-dried at 50 °C for 3 h. Dray-black powders were obtained.

X-ray powder diffraction (XRD) pattern was carried out on a Rigaku Dmax- γ A X-ray diffractometer with Cu K_{\alpha} radiation (λ =1.54178 Å). The morphology of GaP was examined from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg K_{\alpha} X-rays as the excitation source. The ultraviolet and visible light (UV–vis) spectra and photoluminescence (PL) spectra were recorded on JGNA Specord 200 (Japan) PC UV–vis spectrophotometer and Hitachi 850 fluorescence spectrophotometer, respectively.

3. Results and discussion

Fig. 1 shows the XRD pattern of the product. All of the



Fig. 2. XPS spectra of the GaP sample.



Fig. 3. TEM images and SAED patterns of the GaP sample.

seven peaks at d-spacings of 3.131, 2.714, 1.921, 1.640, 1.570, 1.361, 1.250 Å can be indexed as cubic GaP ((111), (200), (220), (311), (222), (400), (331)). The lattice constants are a=5.446 Å, in good agreement with a=5.448 Å (JCPDS card# 12-0191). No evidence of Ga₂O₃, NaCl and other impurities are observed.

Further evidence for the formation of GaP and analysis of as-prepared powder's surface nature, the sample was also characterized by XPS spectrum. Higher resolution spectra taken of the Ga2p, Ga3d and P2p regions were shown in Fig. 2. The Ga $2p_{3/2}$ peak (Fig. 2(a)) at 1117.2 eV and Ga 3d peak (Fig. 2(b)) at 19.40 eV are also consistent with the

reference valued for GaP [13,14]. The P2p core (Fig. 2(c)) shows two peaks, one at 129.6 eV corresponding to P from GaP and the other at 133.7 eV corresponding to the oxidized P species [13]. Because of the higher surface areas are much more easily oxidized when they are exposed to air. Thus, the phosphorus atoms on the surface of the product may turn to oxide phosphorus gradually, resulting in the oxidized phosphorus species in the XPS spectrum. Alivisatos et al. have observed the similar phenomenon in InP nanocrystals [15].

The morphology of as-prepared GaP was observed by the TEM. The sample was prepared by placing a drop of



Fig. 4. (a) UV-vis and (b) PL spectra of the GaP sample.

dilute alcohol suspension of GaP that was dispersed by ultrasonication onto a carbon-coated copper grid for observation in an electron microscope. In Fig. 3(a), the material on copper grid mainly exhibits uniform particle with about 20 nm in size. In fact, the XRD pattern shows the material is not whole nanosized by Debeye Scherrer calculation. GaP on copper grid coming from dilute alcohol suspension is only a part of smaller material, so the TEM image shows nanoscale particles. In Fig. 3(b), the diffraction rings from inner to outer, at d-spacings of 3.13, 1.92, 1.64 Å, match hexagonal GaP (111), (220), (311) planes, in good agreement with the XRD results. From Fig. 3(c) it can be seen that the sample also consists of flake-like morphology. The corresponding SAED pattern (Fig. 3(d)) of GaP flakes is consistent with the single crystalline nature.

Fig. 4(a) shows the absorption spectrum of a sample dispersed in ethanol by sonication. The absorption spectrum

as-prepared nanoscale GaP shows a shoulder at 360 nm and a shallow tail that extends out to about 700 nm. Bulk GaP is an indirect semiconductor with an indirect band gap of 2.22 eV (559 nm) and a direct band gap of 2.78 (446 nm). We attribute the steep absorption and shoulder at 360 nm to a direct transition in the GaP quantum dots (QDs); the shallow tail region above 600 nm is attributed to the indirect transition. Micic et al. have researched the similar situation in GaP nanocrystals [16]. Fig. 4(b) shows the room temperature PL spectrum from as-prepared GaP. The excitation wavelength is 230 nm and the filter wavelength is 310 nm. It is clear that one emitting peak enters at 330 nm and this originates from generally intrinsic band gap PL of GaP. Compared with the luminescent spectral behavior of the bulk GaP, the emission feature in PL spectrum is attributed to the presence of defects of either interface or interior in nanocrystalline GaP.

The formation process of GaP may be illustrated as follows:

 $PCl_3 + 3Na \rightarrow P + 3NaCl$

 $Ga + P \rightarrow GaP$

In this reaction, nascent phosphorus is generated in the reaction of PCl₃ (boiling point = 76 °C) by metallic sodium (melting point = 98 °C). Then nascent phosphorus and initial gallium combine to form GaP.

The influences of reaction temperature and reaction time on the formation of the GaP were investigated. If the temperature was lower than 250 °C, the yield of GaP was low. If the temperature is higher than 400 °C, the grain size grew easily up. The reaction time of longer than 6 h at 400 °C did not obviously affect the crystallinity and the yield. However, when reaction time was less than 4 h, the reaction was incomplete.

4. Conclusions

In summary, we have succeeded in synthesizing cubic GaP through a reduction–phosphidation by using Ga, PCl₃ and Na at 350 °C for 6 h. XRD pattern reveals the synthesized GaP crystallined in cubic crystal structure. TEM image shows particle-like polycrystal and flake-like single crystalline. PL spectrum exhibits one peak at 330 nm of the as-prepared nanocrystalline GaP.

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