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溶剂热合成制备纳米 $In_{1-x}Al_xP$ 固溶体

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在160℃下，以1,2-二甲氧乙烷为溶剂和配合剂用溶剂热合成法成功地制得10～12 nm的 $In_{1-x}Al_xP$ 固溶体，固溶度 x 在0～0.55之间。XRD和TEM用以鉴定产物的结构和形貌，XPS给出产物的固溶度和纯度。

关键词： 磷化铟铝 溶剂热合成 纳米半导体
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半导体

SOLVOTHERMAL PREPARATION OF NANOCRYSTALLINE $In_{1-x}Al_xP$ SOLID SOLUTIONS

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0 Introducion

InAlP solid solutions are of interest because they could result in short emission wavelengths (up to 580 nm)[1] and are promising materials for obtaining visible lightemitting semiconductor lasers, which may have wide application in the field of optical information processing systems[2]. Most previous studies focused on the growth of InAlP by MOCVD[3] and MBE[4] by using metalorganic source materials.

The technological importance of InP and its solid solutions makes the investigation of "quantum size effects" in these materials desirable[5]. Usually the preparation of Ⅲ-Ⅴ materials by traditonal solid-state methods requires high temperature and the resulting products are in μm[6]. Recently, there are several new methods of preparing InP nanocrystallines. Methanolysis of $[Cp^*(Cl)InP(SiMe_3)_2]_2$[7] or decomposing of $I_3InP(SiMe_3)_3$[8] has been used to synthesize nanocrystalline InP. But these methods used the toxic and air-sensitive starting materials and the precursors were difficult to obtain.

Hydrothermal process has been widely used to synthesize many kinds of nanocrystalline oxides and sulfides with narrow particle size distribution, phase homogeneity and controlled morphology[9]. A

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similar solvothermal technique was developed to prepare α-Al_2O_3, in which glycol was substituted for water[10].

In this work, nanocrystallines InP and solid solutions of InAlP were successfully prepared through a solvothermal process at 160℃, using 1,2-dimethoxyethane (DME) as the solvent instead of water, since InP and its solid solutions can not be formed in water solution. The process is relatively simple and easy to control, and the sealed system can effectively prevent contamination of the toxic and air-sensitive starting materials.

1 Experimental

The preparation includes two steps. (1) The formation of Na_3P: An appropriate amount of analytical grade yellow phosphorus was washed free of water by using absolute ethanol and toluene respectively, and sodium was free of kerosene by using toluene. Both yellow phosphorus and sodium were used without further purification. Then they were put into a Teflon-liner autoclave of 100 mL capacity immediately after toluene was put into the autoclave up to 75% of the total volume. The autoclave was maintained at 150℃ for 5 hours, then cooled to room temperature naturally. A black precipitate of Na_3P was obtained. (2) The formation of InAlP: The solution of toluene was drawn carefully, then an appropriate amount of 0.02 mol · L^{-1} $InCl_3$ and 0.02 mol · L^{-1} $AlCl_3$ in DME was added in the autoclave. The autoclave was maintained at 160℃ for 12 hours, then cooled to room temperature naturally. The obtained black precipitate was collected and washed with absolute ethanol for several times. The final product was dried in vacuum at 100℃ for 2 hours.

The X-ray powder diffraction (XRD) patterns were recorded on a Japanese Rigaku Dmax γA X-ray diffractometer with Cu$K\alpha$ radiation (λ=1.54178 Å). Transmission Electron Microscopy (TEM) images was taken with a Hitachi H-800 transmission electron microscope. The composition and purity of the samples were investigated by the X-ray Photoelectron Spectra (XPS), which was performed on ESCALAB MKII with Mg $K\alpha$($h\nu$=1253.6 eV) as the exciting source. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C_{1s} to 284.8 eV.

2 Results and Discussions

The XRD patterns, as shown in Fig. 1, show the reflections all corresponding to the cubic InAlP phase. After refinement, the cell constants decrease with increasing Al compositon, from 5.862 Å for InP and 5.821 Å for $In_{0.45}Al_{0.55}P$, are close to the literature value[11].

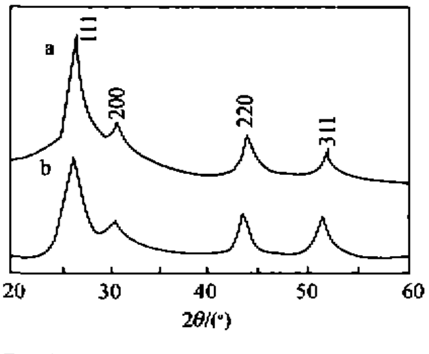

Fig. 1　XRD patterns of the samples
a: $In_{0.45}Al_{0.55}P$　b: InP

Typical TEM microphotographs, as shown in Fig. 2, show particles of InP (Fig. 2a) and a solid solution of InAlP (Fig. 2b). They consist of uniform spherical crystallites and the average size is 10～12 nm.

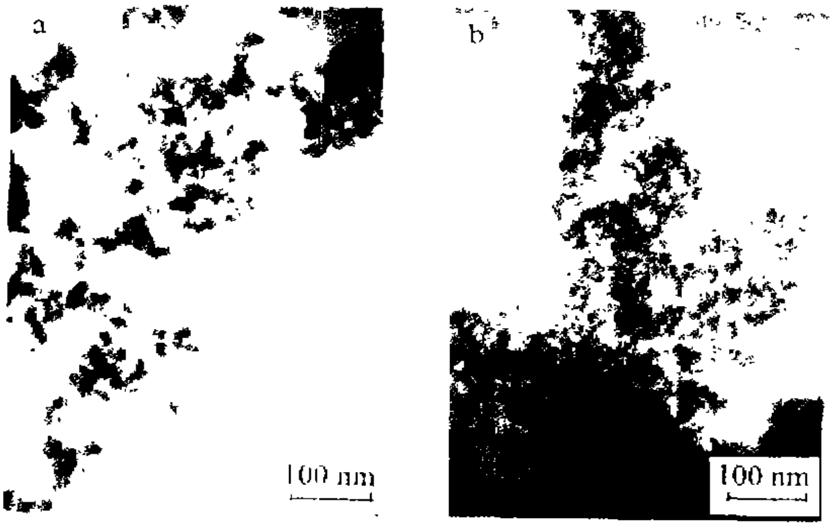

Fig. 2　TEM microphotos of the samples

a: InP　b: $In_{0.45}Al_{0.55}P$

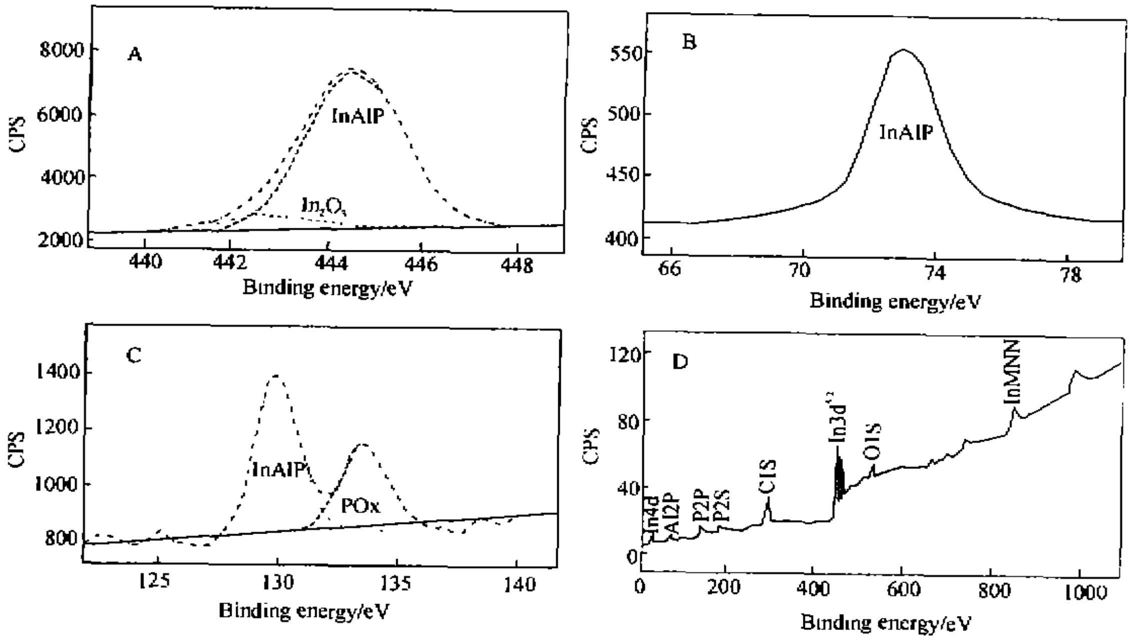

Fig. 3　XPS spectra of $In_{0.45}Al_{0.55}P$

a: In region, showing the $In_{3d_{5/2}}$ peak corresponding to InAlP and In_2O_3

b: Al region, showing the Al_{2p} peaks corresponding to InAlP

c: P region, showing the P_{2p} peaks corresponding to InP and PO_x

d: Survey scan of XPS spectra

Fig. 3 is the XPS analysis performed on the nanocrystalline solid solution of $In_{0.45}Al_{0.55}P$. The composition is quantified by Ga_{3d}、Al_{2p} and P_{2p} peak areas. In Fig. 3a, a curve-fitting analysis of the asymmetrical indium $In_{3d_{5/2}}$ peak shows that there are two signals due to indium-containing species, the larger one at 444. 60 eV from indium in InAlP and the smaller one at 442. 70 eV from indium in In_2O_3. However, the In_2O_3 is not detected by XRD, indicating its content in the sample is less than 5%. In Fig. 3b, the symmetrical aluminum Al_{2p} peak shows that the existence of only one signal at 73. 60 eV, corresponding to InAlP without Al_2O_3(at 74. 50 eV). From the P_{2p} specturm in Fig. 3c, two phosphorus signals are clearly observed. Curve-fitting analysis of these signals indicates two distinct phosphorus environments, one at 129. 90 eV from the InAlP and the other at 133. 60 eV[12] from phosphorus containing oxidized species. The XPS analysis of InAlP (Fig. 3d) also shows the presence of oxygen impurities, however, halogen or alkali metal impurities are not detected and obviously less than that prepared by solid-state methods[6]. Oxygen in the sample is possibly due to exposure to atmosphere since nanocrystalline materials exhibit high surface area to volume ratio.

In the preparation of nanocrystalline $In_xAl_{1-x}P$ solid solutions through solvothermal process, several factors such as temperature, reaction time, the amount of reactants and the kind of solvent should be considered. In the first step, the optimum condition for the formation Na_3P is 150℃ for 5 hours. As an aromatic solvent is essential to prepare sodium phosphide in liquid phase[13], toluene is chosen due to its appropriate boiling point. Furthermore, P and Na can react completely since P can be dissolved in toluene, which elevates the yields of Na_3P. It is observed that at least 20～30% excess yellow phosphorus in toluene solvent is essential to ensure the completely converting Na to Na_3P. The excess phosphorus dissolved in toluene and is removed with the draw of toluene. In the second solvothermal process, the optimum condition for preparing $In_{1-x}Al_xP$ is 160℃ for 12 hours. The higher temperature or longer time has no significant effect on the formation and quality of the products. The byproduct NaCl can be removed by washing with absolute ethanol.

DME acts as both the solvent and the complexing agent due to its capacity for the formation of ionic coordination complexes[14], which may play an important role in the mechanism limiting the growth of particles. Experiments show that merely adduct formation is not sufficient for nanocrystalline $In_{1-x}Al_xP$ formation when using other coordinating solvents such as dioxane. The coordinating solvents must contain no active hydrogen, which is another essential propery; otherwise, the solvent would react with Na_3P and no InAlP solid solutions will be obtained.

Unlike forming a continuous solid solution[1], the solid solubility range of $In_{1-x}Al_xP$ is from $x=0$ to $x=0.55$ in the solvothermal preparation of InAlP solid solutions. We attribute it to the formation of solid solutions of AlP when the ratio of Al is higher, and AlP decomposed when washed with absolute ethanol.

3　Conclusions

Nanocrystalline $In_{1-x}Al_xP$ solid solutions were successfully synthesized through a solvothermal process, using DME as solvent and complexing agent. XRD identified the InAlP phase and TEM microphotographs showed the spherical particles with 10～12 nm in diameter. The XPS analysis gave the composition and the purity of the samples. The solid solubility range was determined to the from $x=0$

to $x=0.55$.

References

[1] Hino I., Suzuki T. *J. Cryst. Growth*, 1984, 68, 483.

[2] Hino I., Kobayashi K., Suzuki T. *Jpn. J. Appl. Phys.*, 1984, 23, L746.

[3] Asahi H., Kawamura Y., Nagai H. *J. Appl. Phys.*, 1982, 52, 4928.

[4] Suzuki T., Hino I., Gomyo A. et al *Jpn. J. Appl. Phys.*, 1982, 21, L731.

[5] Sandroff C. J., Harbison J. P., Ramesh R. *Science*, 1989, 245, 391.

[6] Treece R. E., Macala G. S., Rao L. *Inorg. Chem.*, 1993, 32, 2745.

[7] Douglas T, Theopold K. H. *Inorg. Chem.*, 1991, 30, 594.

[8] Wells R. L., Aubuchon S. R., Kher S. S. *Chem. Mater.*, 1995, 7, 793.

[9] Xie Yi, Qian Yitai. et al *Mater. Sci. & Tech.* B1995, 34, L1.

[10] Inoue M., Tanion H. et al *J. Am. Ceram. Soc.* 1989, 72, 352.

[11] Addamiano A. *J. Am. Chem. Soc.*, 1960, 79, 1537.

[12] Wagner C. D. *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation: Minnesota, 1979.

[13] Peterson D. J., Logan T. J. *Inorg. Nucl. Chem.*, 1966, 28, 53.

[14] Wilkinson G. Ed *Comprehensive coordination Chemistry*, Vol. 3, Pergamon Press: Oxford, 1987, Chap. 24～25.