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Synthesis of Nanocrystalline Iron Monoarsenide via a Reductive Recombination Pathway

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Nanocrystalline FeAs was prepared with $FeCl_3$ and $AsCl_3$ as the reactants and Zn as reductant via a reductive recombination pathway in the temperature range of 150–180°C. The XRD pattern indicated the products were the single phase of iron monoarsenide. A TEM image showed the average size of the FeAs was about 20 nm. XPS gave the ratio of Fe to As 50.9:49.1. The influence of reactions and the possible reaction route of the formation of iron monoarsenide are discussed. © 1999 Academic Press

Key Words: **iron monoarsenide; reductive recombination pathway; nanocrystalline materials.**

INTRODUCTION

Compound semiconductors, mainly metal pnictides, have a wide variety of applications such as satellite TV receivers (1), optical fiber communications, (2) and compact displayers (3–4). Iron arsenides as technologically important as semiconductors (5–7), secondary high-temperature batteries, (8) and catalysts (9) have attracted scientists' attention for a long time. In addition to many other transition metal arsenides, FeAs exhibits the orthorhomic B31 (MnP) structure with cell constant $a = 5.4361$ Å, $b = 6.0242$ Å, $c = 3.3724$ Å, $A = 0.9023$, $C = 0.5595$ (10).

Conveniently, transition metal arsenides could be prepared by direct combination from the element metals and arsenic melted in an evacuated quartz tube and quenched at 900°C (11). The thin film of a transition metal film could be prepared from the metal-organic chemical vapor depositions of metal-organic precursors (12). Recently, Parkin *et al.* synthesized a series of metal arsenides by solid state metathesis (SSM) reactions with metal pnictides and metal halides as precursors at a typical temperature of 500°C; however, only a mixture of FeAs and Fe_2As was reported to be obtained by this method (13–15).

In order to alleviate the time and energy cost, some new approaches have been introduced to prepare inorganic materials, such as the solvent–thermal synthesis (16–18). In the process, starting materials can be solved in the solution and therefore reaction can overcome the solid state diffusion barrier, enabling the reactions to take place at a much lower temperature. In this paper, the single phase of iron monoarsenide was synthesized via a solvent–thermal reductive process using Zn as the reductant in absolute ethanol in the range of 150–180°C.

EXPERIMENT SECTION

Because $AsCl_3$ is toxic and susceptible to hydrolysis, all of the manipulations were carried out in a dry-box, which was filled with nitrogen gas.

In a typical reaction, 0.01 mol anhydrous $FeCl_3$ (99.5%, Shanghai Chemistry Co.) and 0.01 mol $AsCl_3$ (Aldrich Chemistry Co., Ltd.) were put into a Teflon-lined autoclave with 100 ml capacity, and then 75 ml absolute ethanol (99.5% purity, Shanghai Chemistry Co.) and 4.71 g Zn (99.5% purity, Shanghai Chemistry Co.) powder were added. The autoclave was sealed and maintained at 150°C for 12 h, then cooled to room temperature naturally. After washing with absolute ethanol, 0.1 mol/L HCl solution, and distilled water, a black precipitate was collected. The final product was dried in a vacuum box at 80°C for 4 h.

In order to understand the route of formation of FeAs, $FeCl_3$ and absolute ethanol were replaced by $FeCl_2 \cdot 4H_2O$ (Shanghai Chemistry Co.) and benzene (Shanghai Chemistry Co.), respectively (see Table 1).

The X-ray powder diffraction (XRD) pattern was recorded on a Japan Rigaku γA X-ray diffractometer using Cu$K\alpha$ ($\lambda = 1.54178$ Å), employing a scanning rate of $0.05\ \mathrm{s}^{-1}$ in the 2θ range from 10°–70°. A transmission electron microscope (TEM), with an accelerating voltage of 200 KV was used. The X-ray photoelectron spectrum (XPS) was performed on a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonchromatized Mg$K\alpha$ X-ray as the excitation source.

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TABLE 1
Reaction Conditions for the Formation of FeAs

Reaction	Reagents	Other reagent	Solvent	Temp (°C)	Time (hr)	Product
1	$FeCl_3 + AsCl_3$	Zn	ethanol	150–180	12	FeAs
2	$FeCl_2 \cdot 4H_2O + AsCl_3$	Zn	ethanol	160	12	FeAs
3	$FeCl_3 + AsCl_3$	Zn	benzene	160	12	no FeAs

RESULTS AND DISCUSSION

The XRD pattern of the sample as-prepared in reaction 1 is shown in Fig. 1. All the peaks can be indexed as the orthorhombic FeAs phase which is consistent with the literature (JCPDS CARDS No. 12-799). The average crystalline size determined by the Scherrer equation based on the XRD half-width is in the range of 15 nm. The XPS pattern of the sample also confirms the formation of FeAs (see Fig. 2). Two strong peaks at 44.45 and 711.3 eV correspond to As3*d* (Fig. 2a) and Fe2*p*3 (Fig. 2b), respectively in the FeAs phase. From the XPS pattern, the qualification of peaks gives the ratio of Fe to As as 50.9:49.1 which is close to the chemical composition of FeAs.

From the TEM micrograph (Fig. 3), we can see that the FeAs particles consist of uniform spherical crystallites and the average size is about 20 nm, which is consistent with that from the XRD pattern.

The optimum conditions for synthesizing nanocrystalline FeAs are in the range of 150–180°C for 12 h. As the temperature is lower than 140°C or the time is less than 4 h, the formation of FeAs is incomplete or even cannot be initiated. However, with the temperature higher or the reaction time longer, the size of the as-prepared particles would become larger.

The actual route may be a reductive recombination pathway in which the components are reduced to the elements.

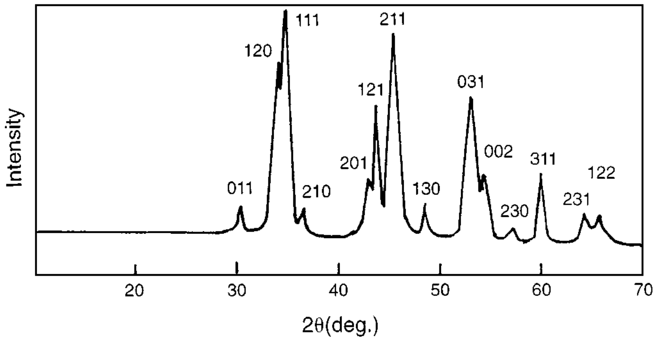

FIG. 1. XRD pattern of FeAs prepared by the reaction of anhydrous $FeCl_3$ and $AsCl_3$.

The process may be as follows:

$$Zn + 2CH_3CH_2OH \Leftrightarrow Zn(OCH_2CH_3)_2 + 2H \quad [1]$$

$$FeCl_3 + AsCl_3 + 6H \rightarrow FeAs + 6HCl \quad [2]$$

$$Zn(OCH_2CH_3)_2 + 2HCl \rightarrow ZnCl_2 + 2CH_3CH_2OH. \quad [3]$$

So the overall reaction can be expressed as

$$FeCl_3 + AsCl_3 + 3Zn \rightarrow FeAs + 3ZnCl_2. \quad [4]$$

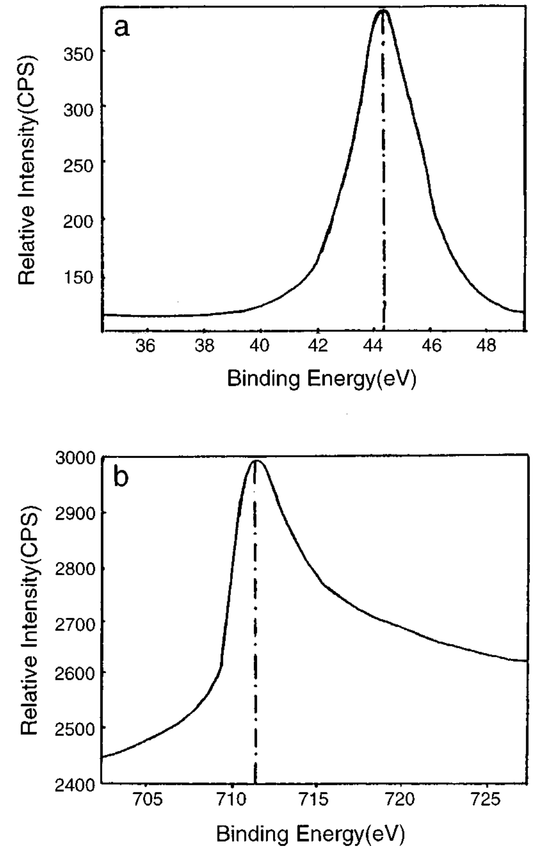

FIG. 2. XPS pattern of as-prepared FeAs products. (a) As3*d* peak of the as-prepared FeAs. (b) Fe2*p*3 peak of the as-prepared FeAs.

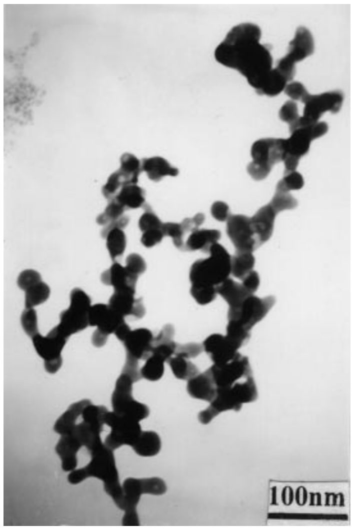

FIG. 3. TEM image of the obtained products FeAs.

This route can be confirmed by the following reactions. If $FeCl_2 \cdot 4H_2O$ was used as the starting material instead of anhydrous $FeCl_3$, similar results were obtained (reaction 2). The crystal water of the iron chlorides is not a serious problem for $AsCl_3$; actually it can also react with Zn to produce reductive agents (17).

We used benzene as the solvent (reaction 3); no phase of FeAs could be obtained. So ethanol not only acts as solvent but also reacts with Zn to produce active hydrogen in the autoclave (19). There are other reasons to choose absolute ethanol as the solvent in the reaction. First, the critical temperature of ethanol is 243°C which is much lower than that of water (374°C) (20), the diffusion of the ions at intermediate temperature (140–180°C) will be more rapid than that in water because of its markedly lower viscosity. This is beneficial to the solubilization of the starting materials and subsequent crystal growth. Second, the hydrolysis reaction of $AsCl_3$ restricts the use of water as a reaction medium in the solvent-thermal process. But ethanol does not have this problem. Because the tendency of alcohol to self-ionize is significantly less than that of water ($PK_{auto}(C_2H_5OH) - PK_{auto}(H_2O) = 5.1$) (21), the participation of the alcohol in the solvolysis reaction is less pronounced, thought it can with Zn at high temperature.

In order to bring the reaction to completion, the amount of Zn powder should be in excess of 20%. The residue of Zn powder can be removed by washing with dilute HCl (0.1 *M*) solution.

CONCLUSION

In this paper, we successfully prepared a nanocrystalline iron arsenide semiconductor through the reaction of $FeCl_3$ and $AsCl_3$ via a reductive recombination process. The final products were characterized by XRD, XPS, and TEM. We also discussed the possible chemical formation process of FeAs.

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