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Phase Relations in the Si–$ZnAs_2$ System in the Range 45–100 mol % $ZnAs_2$

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Abstract—The Si–$ZnAs_2$ pseudobinary join of the Zn–Si–As system has been studied using physicochemical characterization techniques. It contains a congruently melting compound of composition $ZnSiAs_2$ and has two eutectics: Si–$ZnSiAs_2$, at 55 mol % Si + 45 mol % $ZnAs_2$, with the melting point at 1010°C, and $ZnSiAs_2$–$ZnAs_2$, at 93 mol % $ZnAs_2$ + 7 mol % Si, melting at 730°C. The solubilities of the end-members in $ZnSiAs_2$ are within 1 mol %.

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INTRODUCTION

There is currently considerable interest in the new field of solid-state electronics that relies on the possibility of spin-oriented electron transfer from a ferromagnet to a nonmagnetic semiconductor, which is expected to evolve into single-electron logic circuits and spin information systems in which an electron's spin will serve as a memory cell: one spin, one bit [1]. Spin-polarized electron injection from ferromagnetic metals ensures spin polarization within 10%. At cryogenic temperatures, higher degrees of polarization, up to 100%, can be achieved in semiconductor–EuO and semiconductor–cadmium chromium chalcogenide spinel (magnetic semiconductor) structures. Devices that require cryogenic temperatures are, however, inconvenient for practical application. Moreover, serious difficulties have been encountered in attempts to produce low-resistance ferromagnetic/semiconductor contacts. It is believed that good electrical contacts and high electron polarization can be achieved by creating a diluted magnetic semiconductor (DMS) with a Curie point above room temperature, structurally matched to the known semiconductors. Doping with transition metals (Mn, Cr, Fe) is thought to be the most attractive way of producing DMS's. The best results have been obtained with $Ga_{1-x}Mn_xAs$ nanofilms grown by molecular beam epitaxy. The films were ferromagnetic, with a Curie temperature $T_C < 170$ K [2]. Spintronics requires DMS's with T_C above room temperature. In recent studies, manganese-doped II–IV–V_2 chalcopyrites, in particular $CdGeAs_2$ and $ZnGeAs_2$, were found to have T_C's of 355 and 367 K, respectively [3, 4].

In this work, we focus on another II–IV–V_2 compound semiconductor: zinc silicon diarsenide, $ZnSiAs_2$. The choice of this compound was prompted by the fact that $ZnSiAs_2$ is lattice-matched to Si: even though they crystallize in different symmetries, the (001) lattice mismatch between $ZnSiAs_2$ and Si is below 2%. This suggests the possibility of epitaxial growth.

EXPERIMENTAL

To optimize $ZnSiAs_2$ synthesis conditions, we studied the Zn–Si–As ternary system. Analysis of the Zn–As, Si–As, and Si–Zn constituent binaries [5] indicates that the most likely pseudobinary joins in the Zn–Si–As system are Si–$ZnAs_2$ and Zn–$SiAs_2$. Based on the physicochemical properties of the end-members of these joins, the optimal approach to $ZnSiAs_2$ synthesis is to react $ZnAs_2$ and Si. The choice of these reactants is prompted by the fact that, in contrast to $SiAs_2$ ($t_m = 977$°C), $ZnAs_2$ melts congruently, at a much lower temperature ($t_m = 771$°C), which enables reproducible $ZnAs_2$ synthesis. In addition, the use of $ZnAs_2$ + Si mixtures ensures a lower arsenic vapor pressure in comparison with other starting mixtures and, hence, smaller deviations from the stoichiometry of the ternary compound.

The starting materials for the synthesis of Si–$ZnAs_2$ samples were silicon (Kr-0000) and presynthesized $ZnAs_2$. Zinc diarsenide was prepared as described elsewhere [6], via direct melting of high-purity single-crystal zinc and arsenic.

Table 1. Phase compositions of Si–$ZnAs_2$ alloys (DTA, XRD, and microstructural analysis results)

Composition, mol %	t_e, °C	t_L, °C	Phase composition
$ZnAs_2$	–	771	$ZnAs_2$
97% $ZnAs_2$ + 3% Si	730	760	$ZnAs_2$ + $ZnSiAs_2$
93% $ZnAs_2$ + 7% Si	732	–	$ZnAs_2$ + $ZnSiAs_2$*
90% $ZnAs_2$ + 10% Si	725	807	$ZnAs_2$ + $ZnSiAs_2$
85% $ZnAs_2$ + 15% Si	738	885	$ZnAs_2$ + $ZnSiAs_2$
80% $ZnAs_2$ + 20% Si	740	900	$ZnAs_2$ + $ZnSiAs_2$
70% $ZnAs_2$ + 30% Si	725	1010	$ZnAs_2$ + $ZnSiAs_2$
60% $ZnAs_2$ + 40% Si	740	1060	$ZnAs_2$ + $ZnSiAs_2$
52% $ZnAs_2$ + 48% Si	–	1080	$ZnSiAs_2$
50% $ZnAs_2$ + 50% Si	–	1096	$ZnSiAs_2$
48% $ZnAs_2$ + 52% Si	–	1050	Si + $ZnSiAs_2$
45% $ZnAs_2$ + 55% Si	1010	–	Si + $ZnSiAs_2$

* Eutectic.

The synthesized zinc diarsenide and silicon were thoroughly ground and mixed. The mixtures were placed in ampules, which were then pumped down to a residual pressure of 10^{-3} Pa and sealed off. The samples were synthesized in several steps. First, the temperature was raised to the melting point of $ZnAs_2$ (771°C) and maintained there for 24 h. Next, the samples close in composition to $ZnSiAs_2$ were heated to its melting point (1096°C). The other samples were heated to 10–20°C below this temperature and held there for at least 8 h in order to homogenize the mixtures. After that, the samples were furnace-cooled.

Phase relations were studied by differential thermal analysis (DTA), X-ray diffraction (XRD), and microstructural analysis. The chemical composition of several samples was determined by X-ray fluorescence (XRF) analysis.

DTA scans were performed with a PRT-1000M programmed temperature controller (visualization of heating and cooling curves on an Endim XY chart recorder) and NTR-72 pyrometer. The temperature was monitored with a Pt/Pt–Rh thermocouple, which was calibrated against Sn (232°C), Zn (419°C), Sb (630°C), NaCl (800°C), and Cu (1083°C). The reference substance used was calcined Al_2O_3. Heating curves were measured to 1130–1150°C. Weighed amounts (1 g) of the alloys to be studied were placed in graphitized Stepanov vessels, which then pumped down to a residual pressure of 10^{-3} Pa and sealed off. Because of the high primary crystallization temperature of silicon in the composition range 0–40 mol % $ZnAs_2$, we studied for the most part $ZnSiAs_2$ –$ZnAs_2$ samples.

Microstructures were examined on an Epiquant metallographic microscope. Specimens were prepared by grinding and polishing with GOI paste or ASM 3/2, M 0.5/0, and ASM 0.5/1 diamond pastes (RF State Standard GOST 25593-83) and were then boiled in acetone in a flask with a reflux condenser for 10 min. Next, the specimens were then etched with potassium bichromate or a 2 : 15 : 5 mixture of HF, HNO_3, and CH_3COOH for 5–30 s. After etching, the specimens were thoroughly washed with deionized water and acetone or ethanol.

XRF microanalysis was performed on an EAGLE III μ-Probe (Rh-anode tube, $V = 30$ kV, $I = 1000$ mA). Elemental compositions were determined by the fundamental parameters method using EDAX No Standards software. The accuracy in the major components was 5%.

Phase composition was determined by XRD on DRON-1 (Ni-filtered CuK_α radiation), DRON-2, and Siemens Kristalloflex D5000 diffractometers. XRD patterns were collected in the angular range $2\theta = 10°$–$90°$. Interplanar spacings (d) in the alloys studied were compared to those in reference samples and to the JCPDS PDF data for the Zn–Si–As system.

RESULTS AND DISCUSSION

The DTA, XRD, and microstructural analysis results for the Si–$ZnAs_2$ join are summarized in Table 1. Figure 1 presents the melting diagram of this join. The Si–$ZnAs_2$ join is seen to be pseudobinary, with a eutectic phase diagram. It contains a compound of composition $ZnSiAs_2$, which melts congruently at 1096°C. Earlier, its melting point was variously reported to be from 1067 [7] to 1096°C [8]. The Si–$ZnSiAs_2$ eutectic is located at ≈45 mol % $ZnAs_2$ + 55 mol % Si and melts

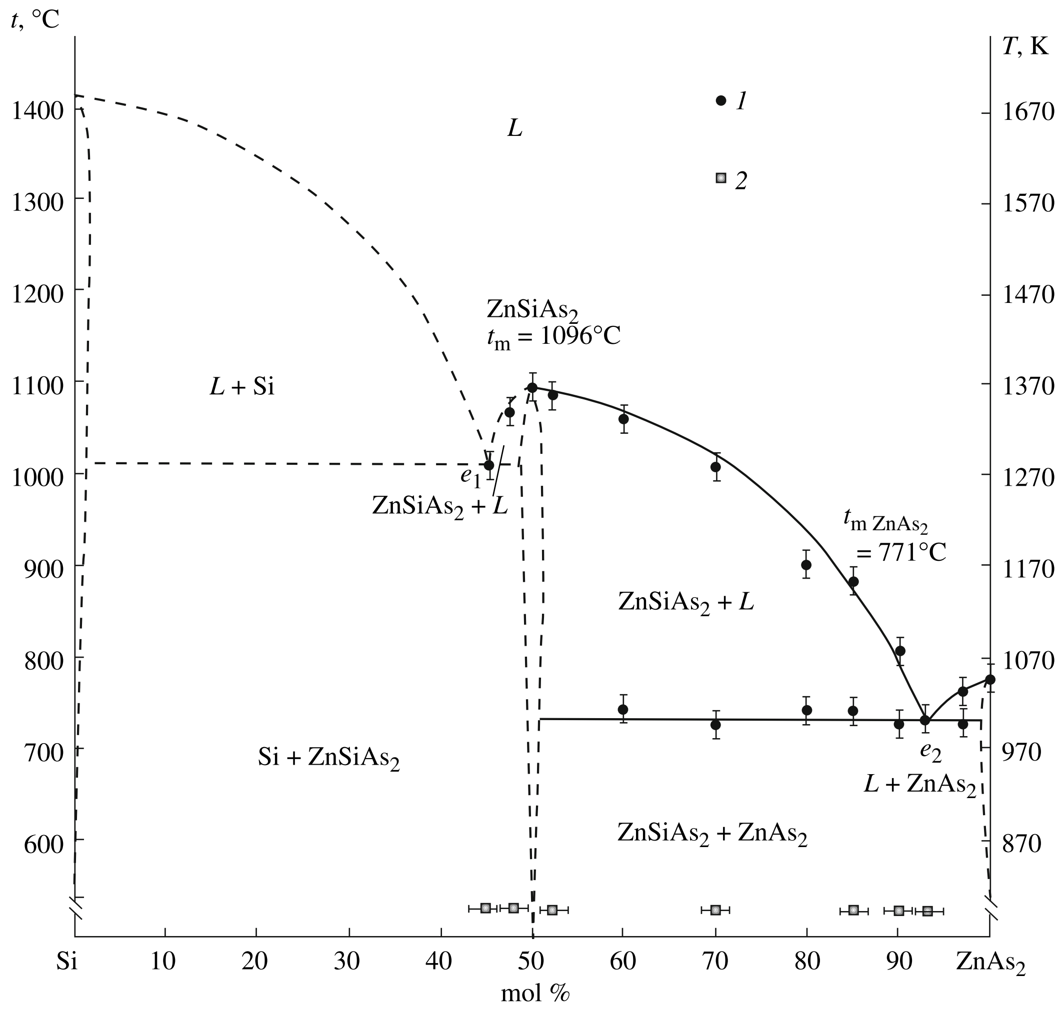

Fig. 1. Melting diagram of the Si–$ZnAs_2$ join: (*1*) DTA data, (*2*) microstructural analysis data.

at 1010°C. The $ZnSiAs_2$–$ZnAs_2$ eutectic is located at 93 mol % $ZnAs_2$ + 7 mol % Si, with the melting point at 730°C. The composition of the latter eutectic was refined by the Tammann method and XRF. Microstructural analysis (Fig. 2) and XRD results confirm that the only phases in the $ZnSiAs_2$–$ZnAs_2$ system below the solidus line are $ZnSiAs_2$ and $ZnAs_2$. The samples represented in Fig. 2 contain $ZnSiAs_2$ (light areas) and the $ZnSiAs_2$–$ZnAs_2$ eutectic (dark areas). The eutectic content has a maximum at 7 mol % Si (Fig. 2a). The XRD results for the Si–$ZnSiAs_2$ samples indicate the presence of only two phases: Si and $ZnSiAs_2$.

Table 2. Lattice parameters of the samples close in composition to $ZnSiAs_2$

Sample.	*a*, Å	*c*, Å	*c*/*a*	*V*, $Å^3$
$ZnSiAs_2$ [8]	5.609	10.878	1.9394	342.23
$ZnSiAs_2$	5.609	10.878	1.9394	342.23
$ZnSiAs_2$ + $ZnAs_2$	5.608	10.888	1.9415	342.42
$ZnSiAs_2$ + Si	5.609	10.883	1.9403	342.39

Zinc silicon diarsenide has a narrow homogeneity range: the Si and $ZnAs_2$ solubilities in $ZnSiAs_2$ are within 1%. This estimate was inferred from microstructural analysis results and from the lattice parameters of the samples close in composition to the ternary compound (Table 2). Their lattice parameters are seen to coincide with those of undoped $ZnSiAs_2$ to within ±0.005 Å and to agree with earlier results [9].

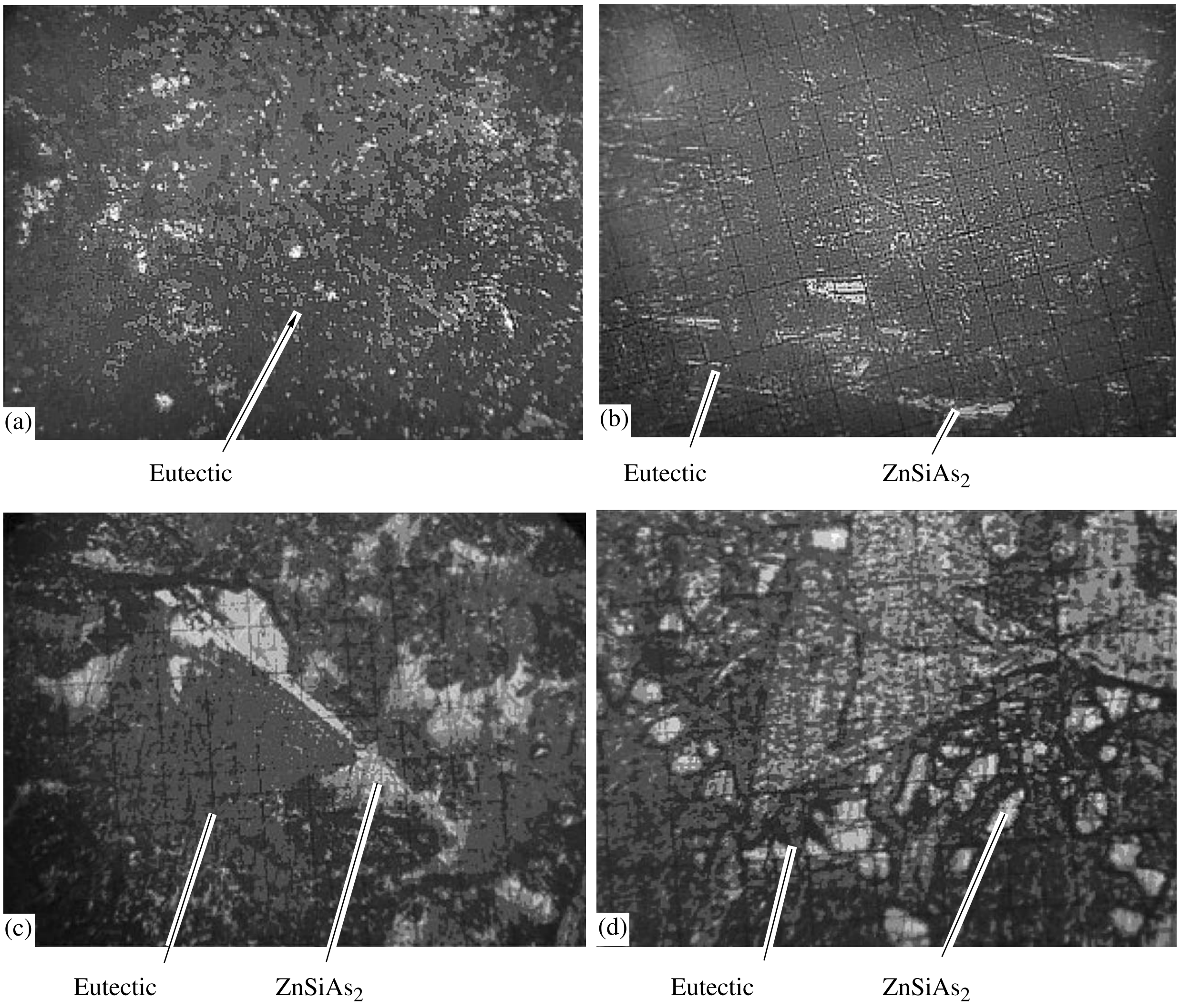

Fig. 2. Microstructures of the Si–ZnAs$_2$ samples containing (a) 7, (b) 10, (c) 20, and (d) 30 mol % Si; 400×.

CONCLUSIONS

The Si–ZnAs$_2$ join was shown to be pseudobinary, with two eutectics. The melting point of the ternary compound ZnSiAs$_2$ was refined, and the Si and ZnAs$_2$ solubilities in ZnSiAs$_2$ were determined to be within 1%. The present phase diagram data will be helpful in optimizing the conditions for the preparation of polycrystals and single crystals of the ternary compound and for the growth of films lattice-matched to silicon.

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