Electrical properties of Ga and ZnS doped ZnO prepared by mechanical alloying

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(Received 5 January 1998; accepted for publication 26 February 1998)

A series of *n*-type ZnO alloys doped with Ga and ZnS were prepared by mechanical alloying. Densities of 95% to 98% of theoretical density were achieved by hot pressing the milled powders at 1000 and 1200 °C, respectively. The electrical resistivity and Seebeck coefficient of alloys containing 0.25–3.0 at. % Ga were characterized between 22 and 1000 °C. The magnitude of the resistivity and Seebeck coefficient at 22 °C ranged from 0.2 mΩ cm and -25 μV/°C for the most heavily doped specimen to 1.1 mΩ cm and -70 μV/°C for the lightly doped material. The alloys exhibit a positive temperature coefficient of resistivity and Seebeck coefficient with a nearly constant slope over the temperature range studied. Thermal diffusivity measurements on a specimen containing 1.0 at. % Ga were performed over the same temperature range. The thermal conductivity appears to follow a T^{-1} dependence, decreasing from 180 mW/cm °C at 22 °C to 82 mW/cm °C at 1000 °C. An estimate of the maximum dimensionless thermoelectric figure of merit, ZT, in this system at 1000 °C gives a value of 0.26, a factor of three to four less than current state-of-the-art materials such as Si–Ge. A significant reduction in thermal conductivity would be required to make these alloys competitive with existing thermoelectric power generation materials. © *1998 American Institute of Physics.* [S0021-8979(98)03011-4]

I. INTRODUCTION

The thermoelectric properties of a material can be expressed by the dimensionless figure of merit Z defined as

$$ZT=\frac{S^2\sigma T}{\kappa},$$

where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, T is the temperature, and the quantity $S^2\sigma$ is defined as the electrical power factor. The figure of merit of an alloy is a measure of its efficiency in converting heat to electrical energy. Doped Si–Ge alloys are the material of choice for high temperature power generation applications, particularly for interplanetary spacecraft power. While these devices have accumulated over 2.5×10^8 device hours without a single failure, efficiency remains relatively low at only about 6%–8%. The search for materials with a higher figure of merit has been an ongoing process in recent years. Oxides have traditionally been disregarded as viable thermoelectric materials due to their large band gap and low electrical conductivity. However, a recent study by Ohtaki *et al.*[1] examined $(Zn_{1-x}Al_x)O$ alloys where $x=0-0.1$ for high temperature thermoelectric applications and reported a dimensionless figure of merit of 0.31 in $(Zn_{0.98}Al_{0.02})O$ at 1000 °C. Tanaka *et al.*[2] have examined various ZnO alloys doped with other oxides for thermoelectric applications and reported a power factor (S^2/ρ) between 1.0 and 3.0 μW/cm K^2 near 1000 °C. Considerable interest has also developed in the application of ZnO thin films for optoelectronic devices such as transparent thermal mirrors and glass coatings. Wang *et al.*[3] examined the electrical properties of transparent thin films based on ZnO doped with Al_2O_3, Ga_2O_3, In_2O_3, and Ge_2O_3 and found that elemental Ga can act as a dopant, thereby increasing the electrical conductivity. A more recent publication by Srikant and Clark[4] examined an anomalous variation in the band gap of ZnO films as the carrier concentration was varied between 10^{18} and 10^{20} cm^{-3}. They attribute this effect to quantum confinement of carriers in fine-grained samples by the presence of large potential barriers at the grain boundaries. The recent interest in the electro-optical properties of ZnO motivated this study of the electrical properties of ZnO doped with Ga. The possibility of isostructural alloying with ZnS provides a mechanism to decrease the lattice thermal conductivity, thereby improving thermoelectric efficiency.

II. EXPERIMENTAL PROCEDURES

Bulk specimens of ZnO with either Ga or ZnS dopant were prepared by mechanically alloying (MA) and hot pressing. The precursor materials consisted of ZnO powder with a stated purity of 4–9's, Ga with a stated purity of 6–9's, and ZnS chunks with a stated purity of 4–9's, all from Johnson-Matthey. Compositions of the samples studied are listed in Table I. MA was carried out by milling the ZnO and additive powders in a Spex 8000 mixer/mill using hardened steel vial and six hardened steel balls. The material was milled for 3 h after which the powder was transferred under high purity helium to a 1.27 cm diameter Mo foil-lined graphite die. The

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TABLE I. ZnO compositions, hot pressing temperatures, and room temperature electrical properties.

Sample ID	Atom % Ga	Atom % ZnS	Pressing temp. (°C)	ρ_0 (mΩ cm)	$n_n(\times 10^{20})$ (cm^{-3})	μ (cm^2/Vs)
ZOG-1	3	—	1000	0.23	5.7	46.7
ZOG-2	1	—	1000	0.25	4.2	60.5
ZOG-3	1	—	1200	0.23	4.29	62.8
ZOG-4	0.5	—	1000	0.51	1.79	68.3
ZOG-5	0.5	—	1200	0.32	2.79	68.4
ZOG-6	0.5	—	1200	0.42	2.13	68.3
ZOG-9	0.25	—	1200	0.77	1.22	65.4
ZOG-10	0.25	—	1000	1.08	0.86	67.3
ZOGS-4	0.5	5.0	1000	0.15	10.0	39.4
ZOGS-5	0.5	1.0	1200	0.38	2.30	69.3
ZOGS-6	0.5	3.0	1200	0.44	2.09	67.4
ZOGS-7	0.5	5.0	1200	0.15	10.80	38.8

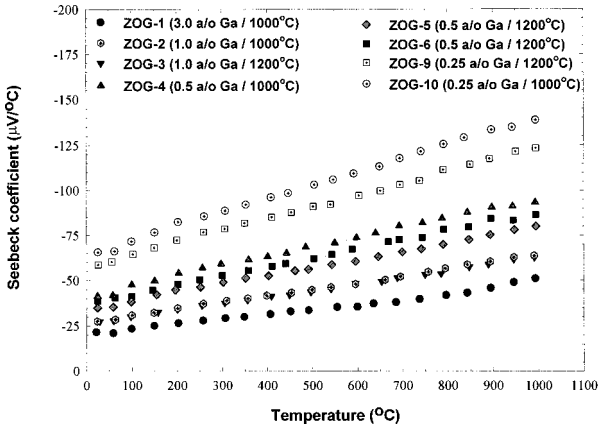

FIG. 1. Temperature dependence of the Seebeck coefficient of Ga-doped ZnO.

die assembly was then positioned in a rf hot pressing chamber. The powders were heated at a rate of 3°–5°/min and were pressed at temperatures of either 1000 or 1200 °C in order to evaluate the effect of pressing temperature on the electrical properties. A pressure of 79 MPa was applied for 1 h in order to consolidate the powders, followed by a furnace cool to ambient. Samples were sectioned from the primary compact and ground for x-ray diffraction analysis using a powder diffractometer (Scintag, USA) and Cu radiation. The pattern for all samples agreed with the calculated pattern for single phase hexagonal ZnO (space group $P6_3mc$). Room temperature carrier concentration and Hall mobility were measured on thin (0.1 cm) disks using the van der Pauw method[5] with four point contacts equally spaced around the perimeter. The procedure described by Ndlela and Bates[6] was used in this study. A magnetic field of 1 T was applied during which time a minimum of four voltage readings were obtained and subsequently averaged for each of the four current directions. The field was reversed and the voltage samplings repeated. The intermediate Hall coefficients were averaged and the carrier concentration was determined from the relation $n=(R_h e)^{-1}$. The accuracy of this technique is estimated at more than 1%. The electrical resistivity and Seebeck coefficient measurements were performed by a standard dc four-point probe technique[7] and by determination of the slope of the thermal emf versus temperature plot[8], respectively. Both properties were measured simultaneously on the same sample in a vacuum chamber ($\sim 10^{-7}$ Torr) in the temperature range of 25–1000 °C by a computer-controlled data acquisition system. A fifth-order polynomial regression was used to calculate the integrated power factors in the temperature range of 300–1000 °C. The thermal diffusivity of a 1.27 cm diameter by 0.1 cm thick disk of one of the Ga-doped samples was measured from 300 to 1000 °C by a standard laser flash diffusivity technique. Briefly, both faces were coated with a thin (30 μm) layer of graphite and the sample was mounted in a low thermal conductivity holder machined from low density ZrO_2. The sample was placed in the center of a BN tube which was wound with Ta wire. This heater assembly was positioned inside a vacuum chamber such that a pressure of less than 10^{-7} Torr was maintained during the characterization. The front surface of the sample was irradiated by a pulse from a ruby rod laser. The zirconia sample holder minimized conductive heat losses from the material and the thermal transient was measured using an InSb detector. Corrections for finite pulse width and heat loss were applied using an in-house computer program. Thermal diffusivity values were calculated for each 5% increase in temperature between 5% and 95% of the maximum value. An average thermal diffusivity was then determined from these values. The thermal conductivity was determined from the product of the thermal diffusivity, density, and specific heat. Values for heat capacity were estimated from Kopp's rule.

III. RESULTS AND DISCUSSION

Nearly fully dense bulk specimens of Ga-doped ZnO were consolidated by hot pressing. Samples hot pressed at 1000 °C achieved 95% of theoretical density (5.68 g/cm^3) whereas those pressed at the higher temperature, 1200 °C, achieved 98% of theoretical density. ZnO is an n-type conductor, as evidenced from the negative value of the Seebeck coefficient. Increasing the amount of Ga from 0.25 to 3.0 at. % decreases the magnitude of the Seebeck coefficient, as shown in Fig. 1. The Seebeck coefficient of the doped ZnO samples monotonically increases with increasing temperature. By comparing the samples containing 0.5 at. % Ga (ZOG-6 at 1200 °C and ZOG-4 at 1000 °C) and those containing 1.0 at. % Ga (ZOG-2 at 1000 °C and ZOG-3 at 1200 °C) it is seen that the hot pressing temperature has a slight impact on the magnitude of the Seebeck coefficient. The implication from this limited data is that lower Seebeck coefficient results from higher hot pressing temperature. This is consistent with the electrical resistivity data which is shown in Fig. 2. The samples exhibit metallike conductivity over the temperature range studied, suggestive of phonon scattering as the limiting conduction mechanism. Characteristic of band-type semiconductors, increasing the amount of dopant in solution decreases the resistivity in these alloys. Additional electrical characterization of these alloys was performed by room temperature Hall effect measurement and the results are summarized along with compositional details in Table I. Carrier concentration values ranged from

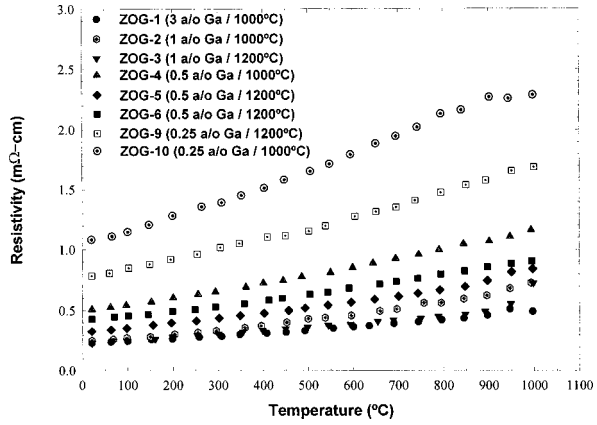

FIG. 2. Temperature dependence of the electrical resistivity of Ga-doped ZnO.

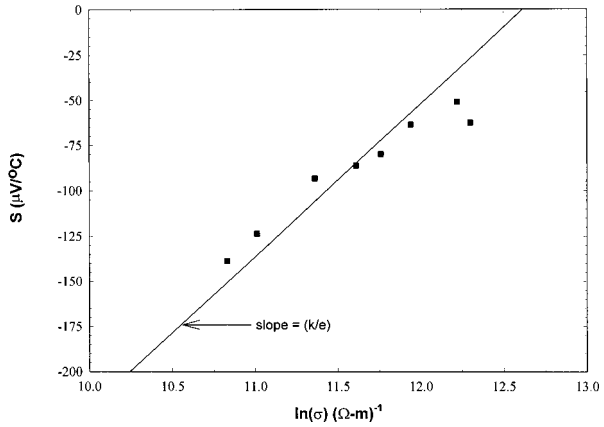

FIG. 4. Jonker plot of Ga-doped ZnO samples at 1000 °C.

0.86×10^{20} cm^{-3} in the sample doped with 0.25 at. % Ga to 5.7×10^{20} cm^{-3} in the sample prepared with 3.0 at. % Ga. One sample, ZOGS-7, was prepared with 5.0 mo. % ZnS in addition to 0.5 at. % Ga and was found to have a carrier concentration of 10.80×10^{20} cm^{-3}, the highest value obtained in this study. The electron mobility values range from 38.8 to 68.5 cm^2/V s, which are unusually high for localized electron, or hopping, conductors. Most oxides have a carrier mobility in the range 0.1–1.0 cm^2/V s. Such large values as obtained on the samples in this study are suggestive of conventional band-type conductivity, as supported by the electrical resistivity and thermopower data.

Results of thermal diffusivity measurements obtained on a 1.0 at. % Ga-doped ZnO sample (ZOG-2) are shown in Fig. 3. The thermal diffusivity continuously decreases over the entire temperature range suggesting that phonon scattering is the dominant mechanism. While the thermal conductivity values indicated are only an estimate, they are expected to be accurate to within about 10% by use of Kopp's rule for C_p. While the conductivity continuously decreases, it is approximately an order of magnitude too high to make this material an attractive high temperature thermoelectric material. The thermal conductivity at 300 °C is estimated to equal 186 mW/cm °C and decreases to 85 mW/cm °C at 1000 °C. These values are comparable to those reported by Ohtaki *et al.* [b] in a sample of ZnO doped with Al_2O_3 to an equivalent composition of 2.0 at. % Al. They reported a thermal conductivity of 402 mW/cm °C at room temperature which decreased to 54 mW/cm °C at 1000 °C. The maximum power factor of the 1.0 at. % Ga-doped ZnO was found to occur at 1000 °C and had a magnitude of ~10 μW/cm $°C^2$ yielding an estimated ZT_{max} of 0.16.

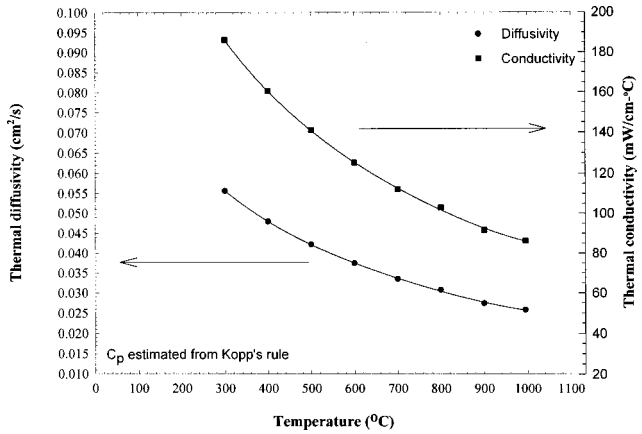

FIG. 3. Thermal diffusivity and estimated thermal conductivity of gallium-doped ZnO.

It is possible to employ these data to estimate the maximum $S^2\sigma$ product in the Ga-doped ZnO system by constructing a Jonker plot[9] of the raw data. Assuming a simple band conductivity model, one can write

$$\sigma = ne\mu, \tag{1}$$

where σ is the electrical conductivity, n is the carrier concentration, e the electronic charge, and μ the carrier mobility. Also, if these materials can be described by simple band theory, then

$$S = \left(\frac{k}{e}\right)\left[\ln\left(\frac{N_E}{n}\right) + A\right], \tag{2}$$

where S is the Seebeck coefficient, k is Boltzman's constant, N_E is the density of states at the Fermi level, and A is the scattering parameter which typically ranges between 0 and 2. By combining Eqs. (1) and (2), one arrives at a simple expression for S in terms of $\ln(\sigma)$:

$$S = \left(\frac{k}{e}\right)\ln(\sigma) - \left\{\frac{k}{e}[\ln(N_E e\mu) + A]\right\}, \tag{3}$$

so that a plot of S versus $\ln(\sigma)$ should be linear with a slope equal to (k/e). Such a plot for the Ga-doped samples investigated in this study at a temperature of 1000 °C is shown in Fig. 4. The linear regression reference line has a slope of (k/e) and, with the exception of one datum at high conductivity (i.e., the 3% Ga-doped specimen), the data fit the linear model reasonably well. This suggests that the above model is a reasonable first approximation and a prediction of $(S^2\sigma)_{max}$ can be used to extract meaningful information about the ultimate potential of these alloys as power generation materials. From the plot, a value of 12.6 is extracted for the logarithm of the intercept [i.e., $\ln(\sigma_o)$] and an $(S^2\sigma)_{max}$ of 11.9 mW/cm $°C^2$ is obtained as shown in Fig. 5, corre-

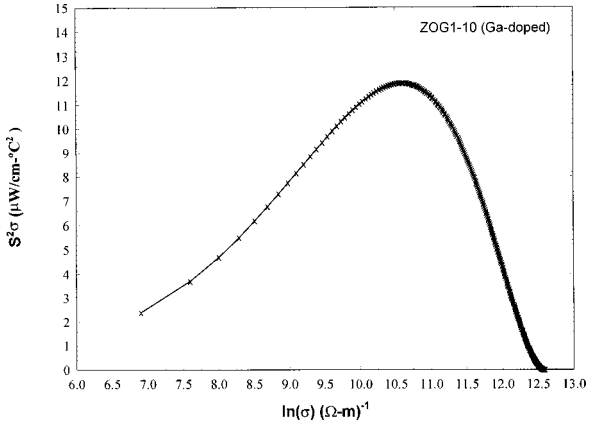

FIG. 5. Predicted ($S^2\sigma$) at 1000 °C of Ga-doped ZnO.

sponding to a resistivity of 2.75 mΩ cm and a Seebeck coefficient of -180.85 μV/°C. Of the samples investigated in this study, a maximum power factor at 1000 °C occurred in the 0.25 at. % Ga-doped specimen (ZOG-10) and had a magnitude of 9.8 mW/cm °C^2. A lower carrier concentration may serve to increase the Seebeck coefficient and hence increase the power factor, albeit the magnitude of the improvement is expected to be modest, at best. Even an optimistic ZT in this system at 1000 °C would be 0.26 which is a factor of three to four less than current state-of-the-art materials such as Si–Ge.

Typically, alloying with an isostructural compound containing a heavier atomic species serves to decrease the lattice thermal conductivity by mass fluctuation scattering. This approach, while highly successful with other alloys such as Si–Ge, is only effective if a large fraction of the heat in the starting material is actually carried by phonons. If most of the heat is transported by carriers, then the alloying method will most likely result in no improvement in ZT. The electronic contribution at a particular temperature can be estimated from the Lorentz equation, $K_l = L_o \sigma T$, where L_0 is the Lorentz number, σ the electrical conductivity, and T the absolute temperature. Assuming the classical Lorentz number of 2.44×10^{-8} W Ω K^{-2}, the polar contribution at 1000 °C is 48.7 mW/cm-K giving a lattice contribution of 37.5 mW/cm K. Therefore, the potential exists for some improvement by incorporating a few percent ZnS. As a test, the thermal diffusivity of one sample containing 5 mole % ZnS, ZOGS-4, was measured within the 300–1000 °C temperature range. When converted to thermal conductivity, the results showed no significant decrease compared with the ZOG-2 specimen, primarily due to the increased carrier concentration (electronic contribution) in the ZOGS-4 material. After accounting for the difference in carrier concentration between these two samples (4.2×10^{20} cm^{-3} in ZOG-2 compared with 10.0×10^{20} cm^{-3} in ZOGS-4), the reduction in lattice contribution at 1000 °C amounts to 36.5% (37.5 mW/cm °C in ZOG-2 compared with 23.8 mW/cm °C in ZOGS-4). Similar approaches which do not contribute to an increase in the electronic component of the thermal conductivity may prove useful. That the ZT in an oxide system is as large as observed in this study is itself noteworthy and suggests that related systems may be worthy of examination.

ACKNOWLEDGMENTS

The Ames Laboratory is operated by Iowa State University for the U.S. Department of Energy under Contract W-7405-ENG82. The ZnO samples were prepared by S. L. Purdum as part of a student research project.

[1] M. Ohtaki, T. Tsubota, K. Eguchi, and H. Arai, J. Appl. Phys. **79**, 1816 (1996).
[2] Y. Tanaka, T. Ifuku, K. Tsuchida, and A. Kato, J. Mater. Sci. Lett. **16**, 155 (1997).
[3] R. Wang, L. H. King, and A. W. Sleight, J. Mater. Res. **11**, 1659 (1996).
[4] V. Srikant and D. R. Clarke, J. Mater. Res. **12**, 1425 (1997).
[5] L. J. Van der Pauw, Philips Res. Rep. **13**, 1 (1958).
[6] Z. Ndlela and C. Bates, Rev. Sci. Instrum. **60**, 3482 (1989).
[7] G. T. Meaden, *Electrical Resistance of Metals* (Plenum, New York, 1965), p. 143.
[8] E. B. Hensley, Phys. Rev. **23**, 1122 (1952).
[9] G. H. Jonker, Philips Res. Rep. **23**, 131 (1968).