Microstructural dependence of electrical transport in bulk $\text{Cu}_x\text{Ge}_{1-x}$ alloys

Satish Vitta *, Shrikari P. Tantri

Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay 400 076, India

Abstract

The electrical transport behavior in bulk processed $\text{Cu}_{78.8}\text{Ge}_{21.2}$ and $\text{Cu}_{77.4}\text{Ge}_{22.6}$ alloys has been studied as a function of temperature. The room temperature resistivity of the alloy with 21.2 at.% Ge was found to be $4.9 \mu\Omega \text{ cm}$, an order of magnitude lower compared to the resistivity of the 22.6 at.% Ge alloy. The resistivity of both the alloys is different compared to thin films of equivalent composition which were prepared by a high temperature solid state reaction process. The difference in behavior is found to be due to the microstructure, volume fraction and morphology of the different phases, which depends on the actual method of processing the material.

Keywords: Microstructure; Electrical transport; $\text{Cu}_x\text{Ge}_{1-x}$ alloys

1. Introduction

The current trend in making integrated circuit devices is to reduce the device dimensions to submicron size so that ultra high density integration can be achieved which facilitates higher speed at low power consumption. This trend is driving materials research to develop interconnect alloys which have not only low electrical resistivity but also low dielectric loss, low diffusivity and high corrosion resistance. Traditionally Al alloys have been used for this application. The electrical resistivity of Cu however is much lower than that of Al alloys and it has higher mechanical strength and electromigration resistance compared to Al alloys. However its fast diffusing nature coupled with the inability to adhere to oxides and other dielectric materials has prevented its usage as an interconnect material. Recently Cu–Ge alloys in the composition range 25–35 at.% Ge were found to have very low electrical resistivity, a factor of three larger than pure Cu, making them highly promising for interconnect application in advanced electronic devices [1–4]. The low electrical resistivity has been attributed to the presence of an ordered ϵ_1 -phase which is predominant in the composition range

25–35 at.% Ge. The alloy thin films in these studies were prepared by a solid state diffusion reaction at high temperature from sequentially evaporated Cu–Ge multilayer structures. Dhar et al.[3] on the otherhand found that ion beam mixing of Cu–Ge multilayers in the solid state results in a two phase mixture with electrical resistivities comparable to those reported by Aboelfotoh and Tawancy [2].

In all the studies mentioned above the crystalline phases in the $\text{Cu}_x\text{Ge}_{1-x}$ alloys were obtained either by annealing at elevated temperatures or by ion beam mixing the low temperature liquid phase, glass. It is however widely known that the crystalline phases that nucleate and grow at high temperatures from the low temperature liquid phase can be different from the crystalline phases that form on cooling the liquid from high temperatures. Hence in the present work the electrical transport behavior of bulk $\text{Cu}_x\text{Ge}_{1-x}$ alloys obtained by solidifying the liquid is studied as a function of microstructure. The compositions studied in the present work lie in the range where the electrical resistivity has been found to decrease with increasing Ge content. Since the Cu–Ge system has a eutectic point at 21.95 at.% Ge, compositions on either side of the eutectic, hypo- and hyper-eutectic were chosen. The $\text{Cu}_x\text{Ge}_{1-x}$ alloys were found to be metallic in nature in agreement with the observations of Aboelfotoh and

Fig. 1. The electrical resistivity ρ of the two $\text{Cu}_x\text{Ge}_{1-x}$ alloys as a function of temperature in the range 10–300 K shows a linear temperature dependence.

Tawancy [2]. However the actual values of electrical resistivity are different compared to the values obtained in thin films of similar composition indicating that the method of preparation and the microstructure play an important role in the electrical transport behavior.

2. Experimental methods

The $\text{Cu}_x\text{Ge}_{1-x}$ alloys were prepared from high purity Cu (99.99%) and Ge (99.999%). The elemental powders were alloyed in the presence of a liquid flux, B_2O_3 using an electromagnetic levitation melting system. The main advantage of using such a system is that it provides an inert atmosphere and a liquid flux substrate on which the liquid solid transformation takes place. The microstructural development as a result of such a transformation will not be influenced by external factors such as oxide layers, substrate/container walls and inclusions [5]. The microstructures resulting from liquid–solid transformation were studied by both optical and scanning electron microscopies. The chemical composition was determined by energy dispersive X-ray (EDX) analysis in the scanning electron microscope. The phase identification was carried out by X-ray dif-

fraction using Cu K_α radiation. The electrical transport behavior in the range 10–300 K was studied using the standard d.c. four terminal resistivity technique.

3. Results and discussion

The electrical resistivity of the different bulk alloys as a function of temperature in the range 10–300 K is shown in Fig. 1. The room temperature resistivity, ρ_{300} of the alloy with 21.2 at.% Ge is $4.9 \mu\Omega \text{ cm}$, about an order of magnitude lower than that of the 22.6 at.% Ge alloy which has a resistivity of $46.2 \mu\Omega \text{ cm}$. The temperature coefficient of resistivity, TCR for the two alloys is 0.005 and $0.09 \mu\Omega \text{ cm K}^{-1}$, respectively (see also Table 1). Aboelfotoh and Tawancy [2] have studied the effect of composition on the electrical transport in thin film $\text{Cu}_x\text{Ge}_{1-x}$ alloys. They find that the room temperature resistivity decreases with increasing Ge content in the range ≈ 15 –25 at.%. The 20 at.% Ge alloy has a resistivity of $\sim 40 \mu\Omega \text{ cm}$ which reduces to $5.5 \mu\Omega \text{ cm}$ for the 25 at.% Ge alloy. The resistivity of the 22.6 at.% Ge alloy studied in the present work is higher than the value obtained for 23 at.% Ge thin film alloy. However the resistivity of the 21.2 at.% Ge alloy is lower by about an order of magnitude compared to the equivalent 20 at.% Ge thin film alloy. Also the electrical resistivity is found to increase with increasing Ge-content, in disagreement with the behavior found in thin films. These results clearly indicate the important role of processing method and the microstructure on the electrical transport behavior in multiphase alloy systems.

The sequence of phase formation during liquid to solid transformation can be determined from the equilibrium phase diagram, Fig. 2 [6]. The pro-eutectic in the 22.6 at.% Ge alloy is the ϵ -phase while that in the 21.2 at.% Ge alloy it is the ζ -phase. The eutectic transformation product in both the cases however is a mixture of ϵ and ζ phases. The pro-eutectic ϵ -phase fraction in the 22.6 at.% Ge alloy is 0.57 with the rest transforming into an eutectic mixture. The total fraction of ϵ -phase in this alloy is ~ 0.9 while the ζ -phase is only 0.1. In the case of the 21.2 at.% Ge alloy the

Table 1

The electrical transport properties together with the microstructural details of the two alloys

Composition (at.% Ge)	Electrical transport			Volume fraction	
	ρ_{300} ($\mu\Omega \text{ cm}$)	TCR ($\mu\Omega \text{ cm K}^{-1}$)	RRR	Pro-eutectic	Eutectic
21.2 (Hypereutectic)	4.9	0.005	1.44	0.15 (ζ)	0.85
22.6 (Hypoeutectic)	46.2	0.09	2.36	0.57 (ϵ)	0.43

c crs = “N N S N” > 0.43

ρ_{300} is the room temperature resistivity and TCR is the temperature co-efficient of resistivity in the range 10–300 K. The residual resistivity ratio, $\text{RRR} = \rho_{300}/\rho_{4.2}$ is determined using the extrapolated value for $\rho_{4.2}$.

Fig. 2. The Cu-Ge binary phase diagram in the range 60–100 at.% Cu.

pro-eutectic ζ -phase fraction is ~ 0.15 . The total ζ -phase including the fraction formed as a result of eutectic transformation is only 0.34 while the ε -phase is 0.66. This difference in the phase mixture together with the morphology of the phases leads to an electrical transport behavior which is different between the two alloys and also when compared to the behavior in thin film alloys which are obtained by a solid state diffusion process. The major constituent in thin films with 20 at.% Ge alloy was found to be the disordered ζ -phase with only traces of the ε_1 -phase. In the case of films with 25 at.% Ge ε_1 was found to be the predominant phase which exhibits the low electrical resistivity [2].

The microstructure of the two alloys was studied both by optical and scanning electron microscopy. The optical microstructure from the 22.6 and 21.2 at.% Ge alloys is shown in Fig. 3(a) and (b), respectively. The 22.6 at.% Ge alloy has a high pro-eutectic ε -phase fraction compared to the ζ -phase fraction in the 21.2 at.% Ge alloy. This pro-eutectic dendritic phase can be seen clearly in Fig. 3(a). The eutectic mixture in both the cases however has a lamellar morphology, which can be seen clearly in Fig. 4(a) and (b), respectively. The lamellar morphology of the eutectic indicates a near equilibrium liquid to solid transformation. The average grain size in both the alloys is ~ 50 – $100 \mu\text{m}$. The average grain size in thin films however was 0.1 – $1.0 \mu\text{m}$, about two orders of magnitude lower than the

grain size in bulk alloys. The ε -phase is unstable below 823 K and undergoes a polymorphic transition to the ε_1 -phase. The low temperature ε_1 -phase has a monoclinic crystal structure [7]. But the crystal structure of the high temperature ε -phase is not known. Hence identification of the phases present in the different alloys was done assuming that the ε -phase transforms completely to the ε_1 -phase below 823 K and that the alloys contains only ε_1 and ζ phases at room temperature. A clear evidence for the solid state transformation of ε – ε_1 phase is seen in Fig. 3(a) which shows the presence of transformation twins in the pro-eutectic ε -phase. The X-ray diffraction spectra from the two alloys is shown in Fig. 5. Both the alloys show the presence of hexagonal ζ -phase and the monoclinic ε_1 -phase. The ε_1 -phase is known to be disordered in nature. However in the case of $\text{Cu}_{75}\text{Ge}_{25}$ alloy thin films the ε_1 -phase is found to be chemically ordered [2]. In the present work both the alloys show peaks in the x-ray diffraction spectra which correspond to the or-

Fig. 3. (a) The proeutectic ζ -phase in the form of dendrites can be seen among the eutectic grains. The volume fraction of the proeutectic phase however is only ~ 0.15 , very small compared to the eutectic which is 0.85. (b) The volume fraction of the large proeutectic ε -phase is ~ 0.57 and can be seen clearly. The high temperature ε -phase undergoes a solid state transformation to the ε_1 -phase leaving behind transformation twins which can be clearly seen in the proeutectic phase.

Fig. 4. The eutectic transformation product has a lamellar morphology indicating a near equilibrium transformation. (a) 21.2 at.% Ge alloy; (b) 22.6 at.% Ge alloy.

dered ε_1 -phase. However a more detailed investigation is needed to conclude the formation of ordered ε_1 -phase in the bulk $\text{Cu}_x\text{Ge}_{1-x}$ alloys.

4. Conclusions

The effect of microstructure, volume fraction of the different phases and their morphology on the electrical transport behavior in bulk $\text{Cu}_x\text{Ge}_{1-x}$ alloys has been investigated. The alloy with 21.2 at.% Ge exhibits a lower resistivity when compared to the 22.6 at.% Ge alloy, in disagreement with the behavior found in thin films. The room temperature resistivity of the bulk 21.2 at.% Ge alloy, $4.9 \mu\Omega \text{ cm}$ is comparable to the value determined for the 25 at.% Ge thin film. The phase mixture in the two cases however is totally different. While the 21.2 at.% Ge bulk alloy consists of only $\sim 66\%$ ε_1 -phase the 25 at.% Ge thin film has only the

Fig. 5. The X-ray diffraction spectra from the two alloys indicates the presence of both the monoclinic ε_1 -phase and the hexagonal ζ -phase.

ε_1 -phase. These results clearly indicate the role of microstructure on the electrical transport behavior in $\text{Cu}_x\text{Ge}_{1-x}$ alloys.

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