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Direct current electrical conductivity of a Ge–Au composite thin film near the critical threshold

Long Ba, Kebin Li, Yong Qin, Zhixiang Chen and Lide Zhang
Institute of Solid State Physics, Academia Sinica, Hefei 230031, People's Republic of China

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Abstract. The Ge–Au polycrystalline film was prepared by room-temperature ageing and thermal annealing with amorphous film. A transmission electron microscopy investigation showed that the Au grains grow from a size of 10 nm in the unannealed sample to a size of 100 nm in the annealed sample. The correlation length was calculated in order to give a description of morphology geometry. The DC electrical resistance was measured over the temperature range of 77–300 K. Percolation theory was used to interpret the conductivity dependence on metal content, which can be expressed as $\sigma_m = \sigma_0(x - x_c)^t$, where x_c is about 50.45% and t is about 1.34 for unannealed samples and 1.55 for annealed samples. The similar electrical conductance of the unannealed and annealed samples shows that the electrical conductivity is not sensitive to the growth of Au grains.

1. Introduction

There have been a considerable number of researches on the electrical conductivity of metal insulator composites in the past decades. Besides many experimental investigations of the metal–perfect insulator (such as cermets [1] and polymers [2]) composite system, there are interesting results on the metal–semiconductor system. The electrical conductivity and metal–insulator transition (MIT) of the Ge–Au system has been investigated by Dodson *et al* [3]. Rosenbaum *et al* [4] have investigated the MIT of a granular Ge–Al thin film near the percolation threshold. For metal–semiconductor composites, metal grains were embedded in the supersaturated semiconductor matrix. The morphology of the film is affected by various methods of film preparation. The material microstructure (grain geometry, grain distribution, phase structure) has an influence on the electric transport characteristics, which may increase the complicity of the elucidation. For a composite system, percolation theory is widely used to interpret the electrical conduction behaviour near the critical threshold. Since an amorphous Ge–Au film can crystallize at a temperature of less than 100 °C, forming a mixture of Ge and Au grains [5], Ge–Au composite films with different Au grain sizes can be prepared by thermal treatment of amorphous Ge–Au film. In this paper, we present an experimental investigation of the DC conductivity of a Ge–Au thin film near the critical threshold. The effect of film morphology to the electrical conductivity near the percolation threshold is discussed by comparing the DC conductivity and film morphology of unannealed and low-temperature annealed samples.

2. Experimental details

The Ge–Au film was prepared by a conventional vacuum evaporation method. The pre-weighed Au and Ge were co- deposited on liquid N_2 cooled substrates. The pressure

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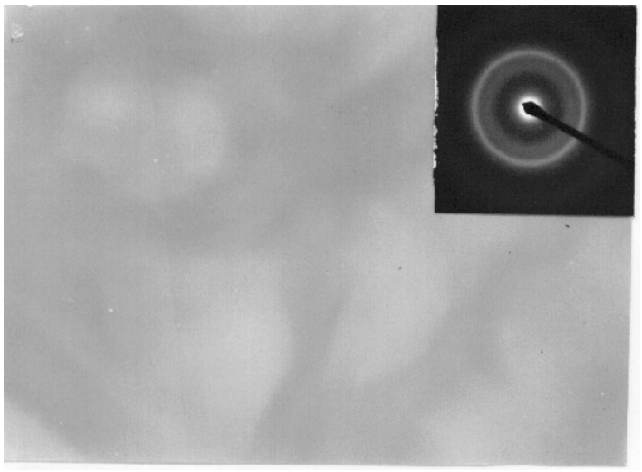
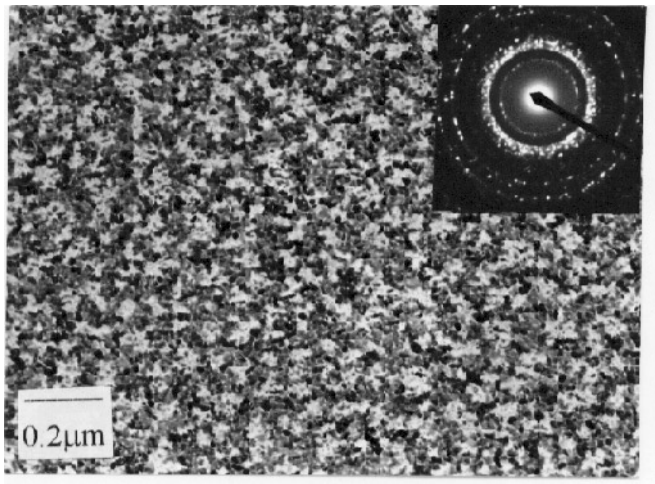


(a)



(b)

Figure 1. The TEM image and SAED pattern of a GE–Au film: (a) as deposited; (b) room-temperature aged.

in the vacuum chamber before deposition is less than 5×10^{-6} Torr. 15 slices of glass with a length of 20 mm and width of 4 mm were used as substrates for electrical conductivity measurement. 15 NaCl substrates were also placed near the glass substrate for microstructure investigation. The vertical distance from substrate level to two tungsten baskets is 100 mm. The distance between the two evaporation sources is 30 mm. Because of the different distances of the two sources from the various substrates, the Au content gradually decreases from the substrates near the Au source to the substrates near the Ge source. The microstructure was investigated using a JEOL 200CX transmission electron microscope with an accelerating voltage of 200 kV. The compositions of 15 samples were measured using an EDAX system attached to an H-800 transmission electron microscope.

The microscopic pictures of annealed samples were digitized using an image processing system. 400×400 binary pixel images were picked out by setting a suitable boundary

threshold to calculate the geometry correlation length ξ and the volume fraction of binary phases x_i. The correlation length is defined as the root-mean-square distance between two pixels in the same cluster, averaged over all finite clusters. The average distance between two pixels in a given cluster as expressed as $R_s^2 = (1/2s^2)\sum_{ij}|\boldsymbol{r}_i - \boldsymbol{r}_j|^2$, where s is the number of sites in the cluster and $r_i - r_j$ is the distance between two sites. The correlation length ξ is R_s averaged by $s^2 n_s / \sum_s s^2 n_s$, expressed as $\xi = (\sum R_s^2 s^2 n_s)/\sum_s s^2 n_s$ and n_s is the number of clusters. For convenience in calculation, we randomly pick 20 clusters with an image resolution of 400×400 pixels. Taking s to be the pixel number, by measuring each R_s, the correlation length ξ can be calculated.

A Solartron 7071 computing voltmeter was used for resistance measurement. Four Ag electrodes 3 mm wide were deposited on each sample for four-electrode measurements. The electrical resistance was measured from room temperature to liquid N_2 temperature. 1 mA constant electric current was applied to all samples. All samples were annealed at 100 °C for 30 min in a vacuum furnace with vacuum pressure of at most 5×10^{-5} Torr. The resistances of annealed samples were measured under the same conditions. The morphologies of annealed samples were also examined using transmission electron microscopy.

3. Results

3.1. Microscopic morphology of unannealed and annealed samples

The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) consists of the GE–55 at.% Au as-deposited sample and a sampled aged for several days at room temperature are shown in figure 1. Since they were deposited on a cooled substrate, most Au atoms in the films were in the amorphous state, as shown in figure 1(a). Because of the high diffusing velocity of Au atoms in the amorphous matrix, the Au atoms will aggregate quickly, causing crystallization of the amorphous alloy, especially in the case of high Au content. The amorphous sample of our experiment can crystallize during short-time, low-temperature annealing or room-temperature ageing, forming the Ge–Au metastable phase and then separating into a mixture of Au, Ge binary phases. Figure 1 shows that most grains grow to the size of about 10 nm after staying at room temperature for more than one week. The morphologies of two samples annealed at 100 °C for 30 min are shown in figure 2. The deviation of thickness of the two samples is within 10%. From the TEM image, sample 1 (see table 1) shows more connected Au grains, while sample 15 shows more isolated Au grains. The SAED patterns indicate that the sample is composed of Au, Ge and a few Ge–Au metastable phases. Table 1 is the EDAX measurement results. Despite the possible error caused by EDAX measurement, this measurement can give a relative composition variation.

Table 1. Au contents (at.%) from EDAX measurement.

Sample No	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Au content	58.2	57.9	57.5	57	56.4	55.7	55	54.3	53.7	53.3	52.5	52.2	51.8	51.6	51.2

From TEM pictures of the annealed samples, the higher the Au content, the more the Au grains connect. The morphology shows that the size of Au grain clusters varies from finite to infinite as the Au content increases. This feature can be described by measuring the correlation length ξ of each grain cluster. The average correlation length ξ and Au, Ge

volume fraction x_i for samples 1, 7 and 15 from 10 picked images were calculated as shown in table 2. Selecting different boundary grey thresholds allows an inaccuracy of about 10%.

Table 2. Average correlation length and volume fraction of three samples.

	x_{Au} (at.%)	Δx_{Au} (at.%)	ξ (nm)	$\Delta\xi$ (nm)
Sample 1	58.6	3.5	∞	
Sample 7	52.2	3.6	89.9	7.3
Sample 15	46.0	2.3	78.2	5.5

3.2. DC measurement results

The plots of high-temperature electrical conductivity data versus temperature for unannealed samples and annealed samples are shown in figures 3(a) and (b) respectively. From conductance σ–T plots, the slope of each set of $\sigma(T)$ data is fitted by linear regression. From the above figures, the slope of the $\sigma(T)$ plot approaches positive from negative, although this variance is small.

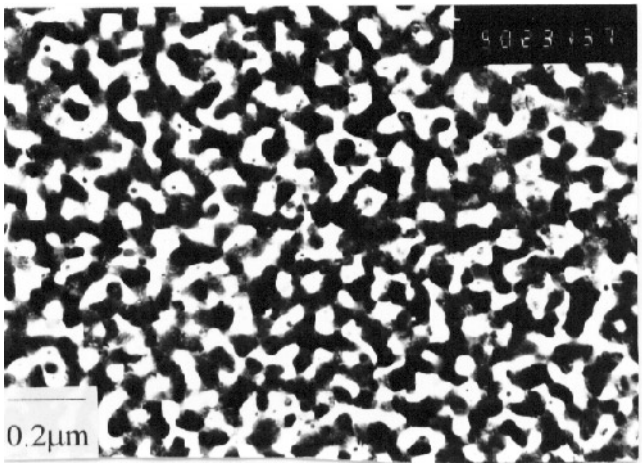
The conductivity versus Au concentration is plotted in figure 4. The $\sigma(x)$ curves for annealed and unannealed samples both show exponential growth at the lower Au content as Au content increases; though more scattered, the conductance content is near constant. As percolation theory predicted, the conductivity will grow exponentially when the conductor component accesses the critical threshold. When $x \geqslant x_c$ and the insulator component is a perfect insulator, the conductivity near the critical threshold can be expressed as $\sigma(x) = \sigma_m((x - x_c)/(1 - x_c))^t$, where σ_m is the conductivity of the metallic component and x_c is the critical content. Both of the $\sigma(T)$ sets of data are fitted by the above expression for the near-exponential growth of conductance at the low Au content, where σ_m is 200 (Ω cm^{-1}). Fitting gives $x_c = 50.45\%$ Au and $t = 1.34$ and 1.55 for unannealed and annealed samples, respectively. The fitting curves were also plotted in figure 4(b).

It was observed that the slope $\mathrm{d}\sigma/\mathrm{d}T$ versus σ increased as the MIT was approached from below for the insulator film, and the slope was roughly constant for the metallic film. From the intercept of the extrapolation of two lines, the σ and the x_c can be determined [4]. The $\mathrm{d}\sigma/\mathrm{d}T$ versus x data for our experimental results were also plotted in figure 5. The solid lines are drawn to guide the eyes. The plots show $\mathrm{d}\sigma/\mathrm{d}T$ values for the two sample groups are very close at lower Au content. The $\mathrm{d}\sigma/\mathrm{d}T$ of the unannealed sample in the higher Au content range is close to zero, while that of annealed is negative.

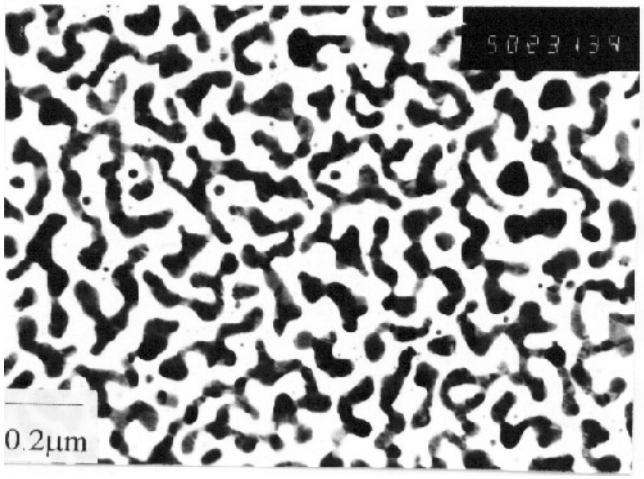
4. Discussion

In the previous study, the MIT of a Ge–Au film at low temperature exhibits a different critical value of x, which is larger for the crystalline phase, and temperature dependence at the transition, which is also larger for the crystalline phase. From the above experiment, room-temperature ageing or thermal annealing causes the amorphous Ge–Au film to crystallize, leading to the growth of Au and Ge grains. The influence of microstructure on DC conductivity requires further understanding of the conductivity microstructure dependence.

TEM shows that the amorphous Ge–Au film quickly decomposes into crystalline Ge, Au composite film with a grain size of less than 10 nm. On isothermal annealing at 100 °C for 30 min the grains grow to a size of about 200 nm. The SAED indicates that there remains



(a)

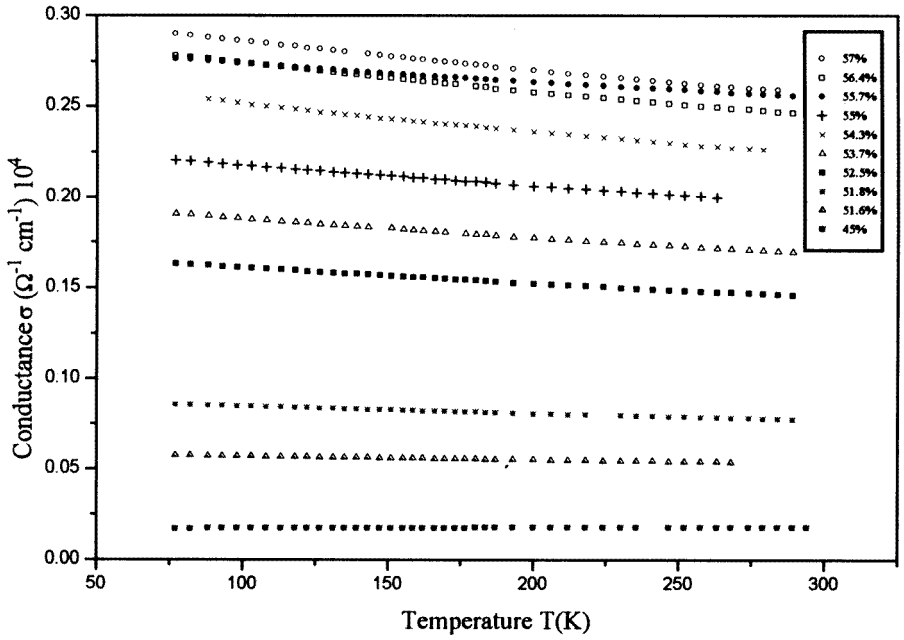


(b)

Figure 2. TEM images of GE–Au films annealed at 100 °C for 30 min: (a) 58.2 at.% Au; (b) 51.2 at.% Au.

Ge–Au metastable phase after room-temperature ageing or thermal annealing (less Ge–Au metastable phase exists in the annealed sample). After room-temperature ageing, most Au atoms dissolved and formed nanosize Au grain aggregation clusters. The different darkness of the Au grains may indicate the incomplete dissolving of Au atoms. Thermal annealing enables the growth of grains. The size and shape of Au grain clusters are sensitive to Au content. More isolated Au grain clusters formed in the sample of lower Au content. With increasing Au content, the Au clusters connected throughout the sample.

Since the morphology is quite similar to a percolation network, description by a percolation network can be applicable. According to percolation theory, the correlation length near the threshold is proportional to $|p - p_c|^{-\nu}$, indicating the cluster size grows exponentially to infinity. We use the correlation length to describe the geometric features of the Au cluster. As shown in the above results, the correlation lengths of the samples 1, 7 and



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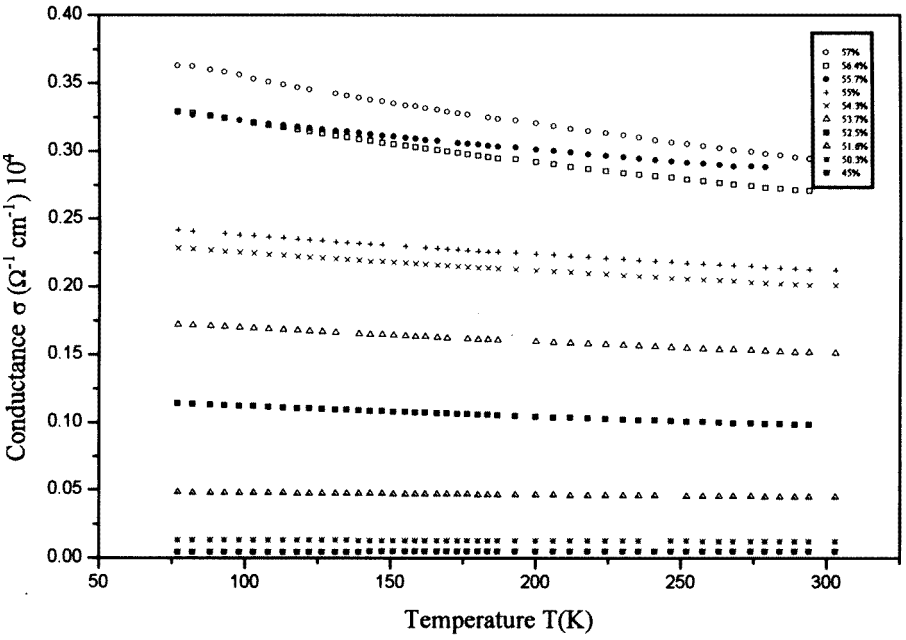
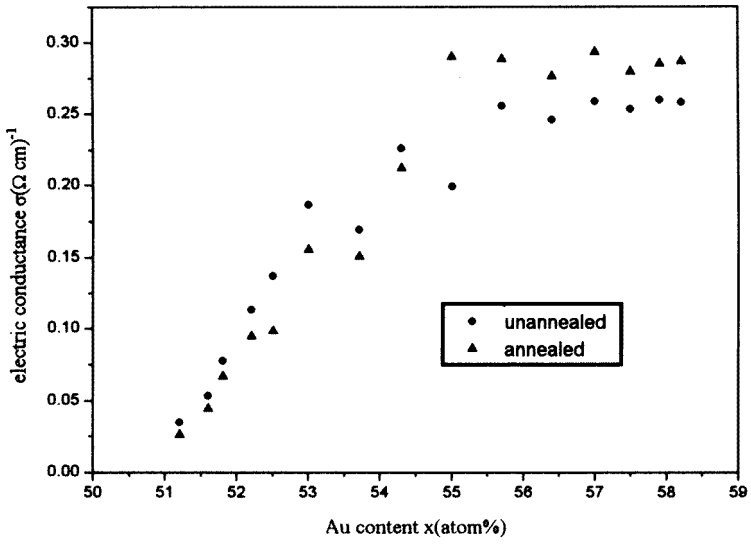
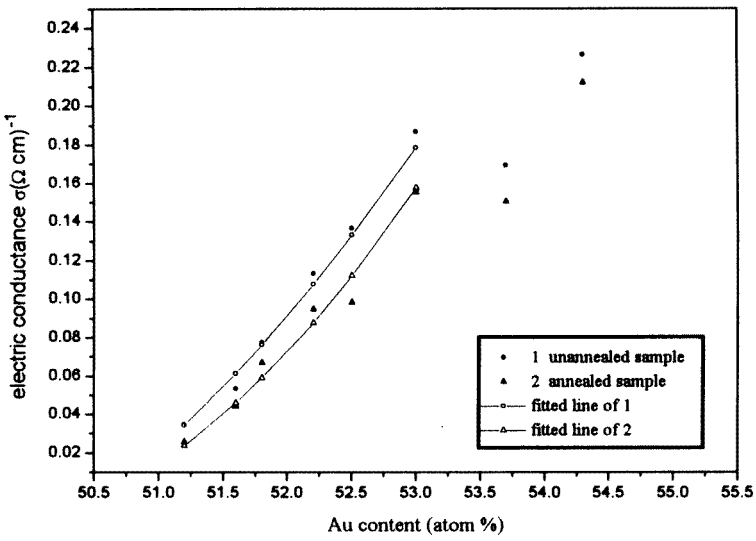


(b)

Figure 3. Electrical conductance data versus temperature plotted over the temperature range of 77–300 K: (a) unannealed samples; (b) annealed samples.



(a)



(b)

Figure 4. (a) Electrical conductance data versus Au content. (b) Fitting lines with the expression of $\sigma = \sigma_0(x - x_c)^t$ for data of lower Au content.

15 are 78.2, 89.9 and ∞, respectively. From the microscopy pictures, similar features can be observed. In the unannealed sample, all Au grains aggregate randomly. After thermal treatment, most Au grains agglomerate, forming grain clusters with different geometric features. The percolation-network-like morphology was found in our annealed sample, with Au grain clusters changing continuously from isolated to connected. Measuring the correlation length of the morphology can provide a description of the percolative geometric

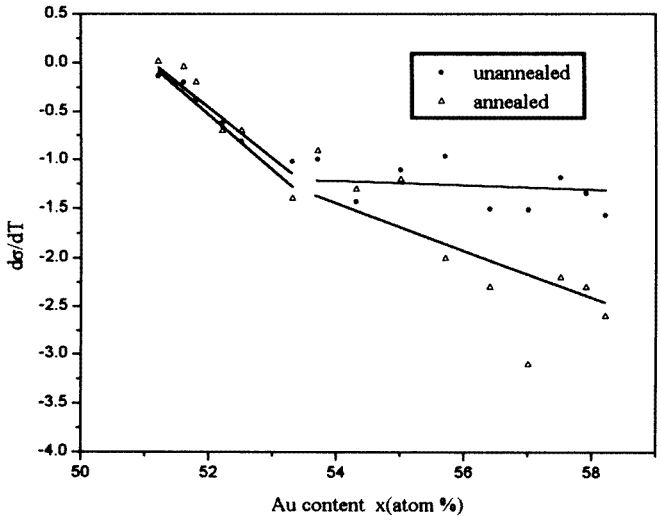


Figure 5. $d\sigma/dT$ versus Au content for unannealed and annealed samples.

features of the Au grain aggregation.

A nanosized metal grain exhibit higher electrical resistance than a larger grain. The resistance–temperature dependence is also reduced with increasing grain size. For the nanosized Au grains dissolved from amorphous Ge–Au phase, Au grains are mixed or enveloped by a Ge matrix, which is supersaturated by Au atoms. Even after thermal annealing, there are also a certain number of Au atoms dissolved in Ge. Most Au grains are contacted or spanned by a Ge layer several Ångströms thick. These increase complexity. When grains aggregate and agglomerate, the distances between grain clusters increase. The conductivity between grain clusters may very between contact carried, tunnelling carried and matrix carried. To interpret phenomenologically the electrical conductivity near the critical threshold, percolation theory is also applicable. Near the critical threshold, the electric conductance exhibits a percolative scaling law.

As shown in figure 4, the plots of σ versus x for annealed and unannealed samples are very similar. The microscopic observation shows that the grain size grew to about 100 nm after thermal annealing. From TEM images, it can be clearly seen that the Au grain clusters connected from a finite size to the infinite network, as Au content increased from 51 at.% to 57.5 at.%. From percolation theory, the GEM equation gives $\sigma_m = \sigma_{hi}[(x-x_c)/(1-x_c)]^{-1}$, for $x \geqslant x_c$ and assuming the insulator conductance equal to zero. Our experimental $\sigma(x)$ data show that the conductivity grew exponentially as Au content increased. Fitting the $\sigma(x)$ data using this equation, the resulting x_c values for unannealed and annealed samples are almost the same. Although considerable grain growth and phase separation take place during annealing, our experiment shows that the effect of microstructure on the percolative behaviour of conductivity is not significant. The effect of microstructure features (such as grain size and conductor geometry) should be investigated for further understanding.

From the detailed discussion for the MIT critical threshold of an Al–Ge granular film, different methods were compared to give the value of x_c [4]. The effect of grain size has not been included in the study. Dodson *et al* [3] compared the low-temperature MIT for amorphous Ge–Au samples and crystalline Ge–Au samples, in the case of Au content less than 28 at.%. The conductivity of an 18 at.% Au amorphous sample is quite similar to

that of a crystalline sample in the temperature range of 300–1.4 K. From the experimental results shown above, the electrical conductance and its temperature dependence are similar for annealed and unannealed samples. Though there are influences such as sample purity and void formation induced by annealing, this experimental study may give evidence that the electrical conductance and its temperature dependence cannot be dramatically affected by grain growth.

Figure 5 shows that the values of $\mathrm{d}\sigma/\mathrm{d}T$ of annealed samples are more negative than those of unannealed samples of higher Au content. This may indicate that the Au aggregation induced by more Au atoms dissolved from Ge after annealing is a response to the more metallic behaviour of the conductivity. As suggested [6], the $\mathrm{d}\sigma/\mathrm{d}T$ versus σ for the insulating and metallic sides of the MIT has a slope on the insulating side and is near constant on the metallic side, taking into account the electron–phonon scattering time. Though our experimental data are somewhat roughly scattered, a two-section feature of $\mathrm{d}\sigma/\mathrm{d}T$ appears, similar to what was discussed by Rosenbaum *et al*.

As discussed above, the morphology change caused by thermal annealing is evident. The similar scaling conductivity behaviour of the unannealed and annealed samples gives an evidence that the conductivity near the critical threshold is insensitive to microstructure. To understanding the fundamental mechanism of the scaling behaviour near the percolation threshold, more experimental work will be required.

In conclusion, the Au grain size of a Ge–Au composite film grows from 10 nm to 100 nm on thermal annealing at 100 °C. The DC conductivities of both samples versus Au content at Au content a little larger than 50.45 at.% show a scaling law. The fitted critical Au content x_c is close to the Au percolative threshold from morphology observation.

Acknowledgments

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