Evidence for superlocalization on fractals in Al/*a*-Ge bilayer films from thermoelectric power measurements

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Temperature-dependent properties of resistivity and thermoelectric power (TEP) were measured in Al/*a*-Ge bilayer films with snowflakelike fractal patterns. We found that the fractals that appeared in the bilayer films have significant influence on the TEP, but little effect on the resistivity. By analysis of the data, it provides possible evidence for the superlocalization of the carriers on fractals in such a bilayer film system, and the superlocalization exponent obtained is about $1.33<\zeta<1.35$, which is approximately in agreement with the theoretical prediction for a fractal system. [S0163-1829(99)07443-3]

I. INTRODUCTION

Hopping conductivity in disordered three-dimensional materials where the wave functions of the electrons at the Fermi level are localized often follows the famous Mott's law $\sigma \propto \exp[-(T_0/T)^{\gamma}]$, with a fixed exponent $\gamma = 1/4$.[1,2] However, in fractal media Levy and Souillard[3] predicted that impurity quantum states and Anderson localized states exhibit superlocalization properties, and their wave functions of electronic states decay faster than exponentially with distance R as $\exp[-(R/L)^{\zeta}]$, with $\zeta > 1$ being the superlocalization exponent and L the localization length (Anderson decay, $\zeta = 1$). The superlocalization exponent ζ is about $1.0 \leqslant \zeta \leqslant 1.14$ for a two-dimensional system and $1.14 \leqslant \zeta \leqslant 1.36$ (Ref. 4) for a three-dimensional system. This specific superlocalization property in fractal media must imply a specific property of hopping conductivity. Deutscher, Levy, and Souillard[5] proposed a thermally activated hopping conductivity law $\sigma_{\mathrm{frac}} \propto \exp[-(T_0/T)^{\zeta/(D+\zeta)}]$, where D is the fractal dimension, and T_0 the characteristic hopping energy of the superlocalized carriers between the superlocalized states.

However, the experimental evidences for superlocalization on fractals are still insufficient. van der Putten *et al.*[6] measured the dc conductivity in conductive carbon-black-polymer composites as a function of temperature. They claimed that their results can be considered as an evidence for superlocalization on fractals, but controversies still remain about the explanation for their data.[7–9] In this paper, we focus our attention on a thin-film fractal system, i.e., metal/amorphous semiconductor (M/a-S) bilayer films. As is known, in the M/a-S bilayer or multilayer films the fractal patterns can be easy to form under some external macroscopic parameters such as irradiation and annealing. A lot of work has been done on the mechanisms of fractal formation experimentally,[10–14] while little progress has been made to elucidate the possible macroscopic physical properties concerning the fractals. In this report, we attempt to investigate the possible effect of the fractal structures on the macroscopic physical properties, such as conductivity and thermoelectric power (TEP) in aluminum/amorphous germanium (Al/*a*-Ge) bilayer film fractal system, and attempt to correlate the fractals and the macroscopic physical properties.

II. EXPERIMENTAL PREPARATION AND MORPHOLOGY OBSERVATION

The Al/*a*-Ge bilayer films used in this work were prepared by evaporating a layer of amorphous Ge and a layer of Al film on a clean glass substrate in vacuum of 2.67×10^{-3} Pa. The bottom layer was *a*-Ge, and the top one was Al. Two groups of samples with different thickness ratios, 30/30 and 25/35 nm, were made, and in each group we made three identical samples simultaneously, and then they were annealed in vacuum at 200 °C for a different time, respectively. By such treatments, snowflakelike fractal patterns were formed in these bilayer films.

Figures 1(a)–1(d), respectively, show the scanning electron microscopy (SEM) pictures for these annealed samples. Photos (a) and (b) are, respectively, for 30/30 nm bilayer films annealed at 200 °C for 80 and 50 min, while (c) and (d) are, respectively, for 25/35 nm bilayer films annealed at 200 °C for 30 and 80 min. It is seen that white ''snowflakelike'' fractal patterns appear due to the crystallization of *a*-Ge. The ''dark'' regions with some small white dots are mainly dominated by Al, where the white dots result from the diffusion of the Ge particles into Al-film, but they do not form fractal clusters. The fractal dimension, D, for these samples was calculated by measuring the fractal dimensions of these snowflakelike clusters using conventional Sandbox-counting method.[15] Since the annealing temperatures can roughly control the morphology of the fractal patterns, the density of the different fractal clusters formed at a given annealing temperature is also approximately uniform at different sites of the sample. The average value of the evaluated dimension D obtained from different regions can be approximately considered as the whole sample's fractal dimension. They are, respectively, about 1.77, 1.84 for two 30/30 nm

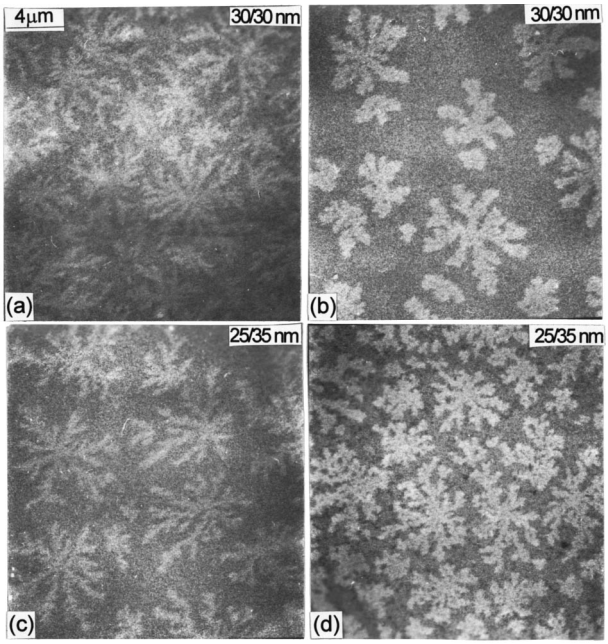

FIG. 1. (a) and (b), respectively, show the SEM patterns for 30/30 nm bilayer films annealed at 200 °C for 80 and 50 min; (c) and (d) are, respectively, for 25/35 nm bilayer films annealed at 200 °C for 30 and 80 min.

bilayer films, and 1.75, 1.81 for two 25/35 nm bilayers.

Temperature-dependent properties of resistivity and thermoelectric power (TEP) were measured in the range 80–300 K using a standard four-probe configuration and the differential technique, respectively. The whole system was automatically controlled by a computer and strictly calibrated by comparison to a standard sample.

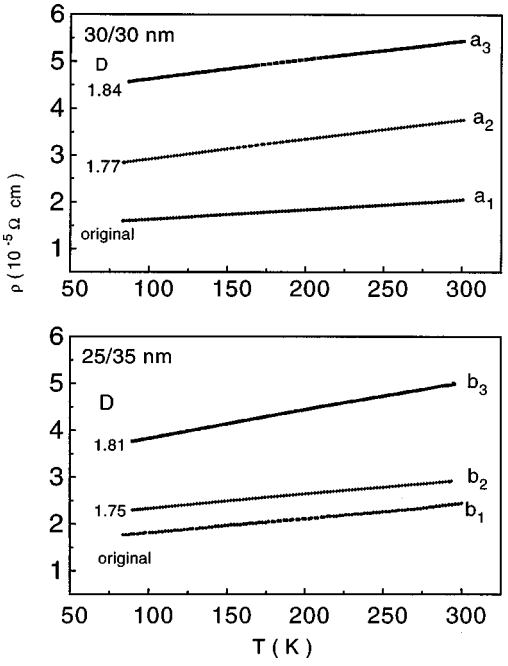

FIG. 2. The resistivity versus temperatures in the range 80–300 K. The curve (a_1) is for the 30/30 nm original bilayer films without fractals, and the curves (a_2), (a_3) are, respectively, for the annealed films at 200 °C for about 80 and 50 min. Similarly, the curve (b_1) is for the 25/35 nm original bilayer films without fractals, and the curves (b_2), (b_3) are, respectively, for the annealed bilayer films at 200 °C for about 30 and 80 min.

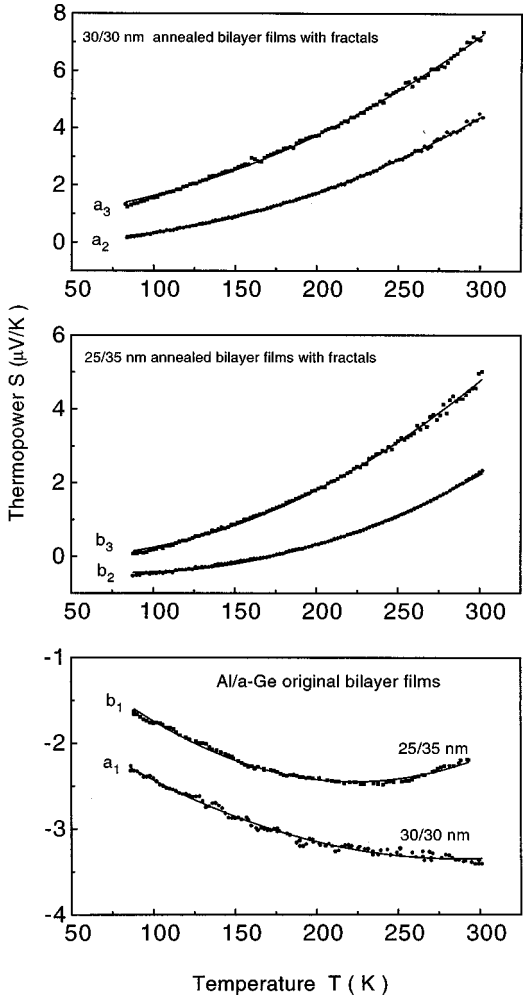

FIG. 3. The TEP versus temperatures in the range 80–300 K; the curves (a_1) and (b_1) are, respectively, for both original 30/30 and 25/35 nm bilayer films without fractals, the TEP is negative over the studied range of T; the curves (a_2), (a_3) and (b_2), (b_3) are, respectively for the annealed 30/30 and 25/35 nm bilayer films with fractal clusters.

III. RESULTS

Figure 2 shows the resistivity versus temperatures for both groups of Al/a-Ge bilayer films. In the top plot, the curve a_1 is for the 30/30 nm original bilayer film without fractal patterns, and curves a_2 and a_3 are, respectively, for the bilayers annealed at 200 °C for 80 and 50 min. Similarly, in the bottom plot, curve b_1 is for the 25/35 nm original bilayer film without fractal clusters, and the curves b_2 and b_3 are, respectively, for the bilayer films annealed at 200 °C for 30 and 80 min. The resistivity for all samples has a linear relation with temperature in the studied range. This means that the conductive properties for all annealed Al/a-Ge bilayer films with fractal clusters still exhibit a metallic behavior, which is similar to that of the original bilayer films. The conduction would be dominated mainly by the conduction, σ_n, of Al conducting channels, the contributions of the car-

TABLE I. Fitting parameters and the calculated superlocalization exponents ζ; the fractal dimension D obtained by the Sandbox counting (Ref. 15) method.

Sample's number	Annealing time at 200 °C	Fitting parameters					
		D	A	B	T_0	α	ζ
30/30 mn	50 min	1.84	-5.25×10^{-1}	3.69×10^{-3}	1050	0.72	1.33
	80 min	1.77	-2.74×10^{-2}	3.01×10^{-3}	1000	0.75	1.35
25/35 nm	80 min	1.81	7.54×10^{-2}	2.58×10^{-3}	700	0.74	1.34
	30 min	1.75	3.79×10^{-1}	1.58×10^{-3}	650	0.77	1.35

riers in Ge semiconducting bands and the carriers on fractals are obviously negligible due to the linear ρ-T relation. Nevertheless, we also noted that the resistivity of the original bilayer films without fractal clusters is always lower than that of the annealed bilayer films with fractals, the magnitude of the resistivity for each group of the annealed samples seems to be significantly enhanced due to the appearance of the fractal clusters. Since the resistivity curves are almost parallel to each other, the enhancement of the resistivity in the annealed samples may originate from the extra scattering of the conductive carriers in Al by the complicated boundaries of fractal clusters or Ge grains diffused into Al regions, this looks like the case of free carriers scattered by impurities or defects.

Figure 3 shows the temperature dependence of the TEP for two groups of samples in the range 80–300 K. In the bottom plot, the curves a_1 and b_1 are, respectively, for the original 30/30 and 25/35 nm bilayer films without fractal clusters, and the TEP is negative over the studied range of T. In the top plot, the curves a_2 and a_3 are, respectively, for the 30/30 nm bilayer films annealed at 200 °C for 80 and 50 min. Similarly, in the middle plot, the curves b_2 and b_3 are, respectively, for the 25/35 nm bilayer films annealed at 200 °C for 30 and 80 min. It is noted that, for all bilayer samples with fractal clusters, the TEP was greatly enhanced and increases monotonically with the increase of temperatures, and meanwhile, the sign becomes positive for both 30/30 nm bilayer films, and for the 25/35 nm bilayer film with $D=1.81$; for the 25/35 nm bilayer film with $D=1.75$, the TEP also become positive above 175 K. These striking properties in the annealed samples are clearly different from those of the original bilayer films without fractal clusters. The results seem to give a strong indication that though the fractals have little effect on the resistivity, they have significant influence on the TEP behavior. The total TEP in the annealed bilayer films would be dominated by multimechanisms and must be considered in detail.

According to the observation of the morphology shown in Fig. 1, the total TEP properties for the annealed bilayer films would be considered as a combination of the contributions of three-band carriers, i.e., the free carriers in the metallic Al conducting bands, the carriers in the Ge semiconducting bands, and the carriers on the fractals which were considered to be superlocalized on the fractals as predicted by the theory.[3] The total TEP should, in general, follow Nordheim-Gorter rule,[16]

$$S_{\text{total}}=(\sigma_n/\sigma_{\text{total}})S_n+(\sigma_s/\sigma_{\text{total}})S_s+(\sigma_{\text{frac}}/\sigma_{\text{total}})S_{\text{frac}}, \tag{1}$$

where S_n, S_s, and S_{frac} are, respectively, the contributions of the free carriers in Al conducting bands, the carriers in Ge semiconducting bands, and the superlocalized carriers on fractals; σ_n, σ_s, and σ_{frac} are, respectively, their conductivity, and $\sigma_{\text{total}}=\sigma_n+\sigma_s+\sigma_{\text{frac}}$. Formula (1) is independent of any specific mechanism of the TEP production. As is well known, the conductivity, σ_n, resulting from the metallic Al band carriers is proportional to the reciprocal of temperature, $\sigma_n\propto 1/T$, the TEP, S_n, can be described by a linear temperature-dependent relation under the energy independent constant relaxation time limitation.[16] Since $\sigma_n\gg\sigma_s$ and $\sigma_n\gg\sigma_{\text{frac}}$, then $\sigma_n/\sigma_{\text{total}}\sim 1$. From Fig. 3 ($a_1$) and ($b_1$), since the TEP in both original bilayer films obviously deviates from a linear relation, this implies that the total TEP in both original bilayer films, S_0, would result from a combination of the free carriers in Al conducting bands and the carriers in Ge semiconducting bands. If one thinks that in the annealed bilayer films with fractal clusters, the scattering mechanisms of the free carriers in the Al conducting channels and the carriers in the Ge semiconducting channels are identical with those in the original bilayer films, the first two terms, $S_{1,2}=(\sigma_n/\sigma_{\text{total}})S_n+(\sigma_s/\sigma_{\text{total}})S_s$, in Eq. (1) can be approximately considered to be proportional to S_0 in the original bilayer films, i.e., $S_{1,2}\propto S_0$. Correspondingly, Eq. (1) can be expressed as $S_{\text{total}}=AS_0+(\sigma_{\text{frac}}/\sigma_{\text{total}})S_{\text{frac}}$, where S_0 can be obtained by fitting the curves a_1 and b_1 in Fig. 3 with polynomial relation, and we get $S_0^{a1}=-1.19-1.50\times10^{-2}T+3.0\times10^{-5}T^2$ and $S_0^{b1}=-0.12-2.09\times10^{-2}T+5.0\times10^{-5}T^2$.

Since the carriers on fractals were supposed to be superlocalized at the Fermi level, the conductivity, therefore, follows $\sigma_{\text{frac}}\propto\exp[-(T_0/T)^{\zeta/(D+\zeta)}]$;[5] the TEP of fractals as predicted by Wang *et al.*[17] follows a power-law relation, $S_{\text{frac}}\propto T^{\theta}$, where $\theta=D/(D+\zeta)$. From $\sigma_n/\sigma_{\text{total}}\approx 1$, we get $\sigma_{\text{frac}}/\sigma_{\text{total}}\propto T\exp[-(T_0/T)^{\zeta/(D+\zeta)}]$, and the total TEP of Eq. (1) can be expressed as

$$S_{\text{total}}(T)=AS_0+BT^{(D/(D+\zeta)+1)}\exp[-(T_0/T)^{\zeta/(D+\zeta)}], \tag{2}$$

where A and B are constant coefficients. If taking $\alpha=\zeta/D$, we get a final expression for the total TEP of Al/a-Ge bilayer films with fractals,

$$S_{\text{total}}(T)=AS_0+BT^{(1/(1+\alpha)+1)}\exp[-(T_0/T)^{\alpha/(\alpha+1)}]. \tag{3}$$

The first term, AS_0, results from the contributions of the free carriers in Al conducting channels and the carriers in Ge semiconducting channels to the TEP, and the second term from the contributions of the superlocalized carriers on frac-

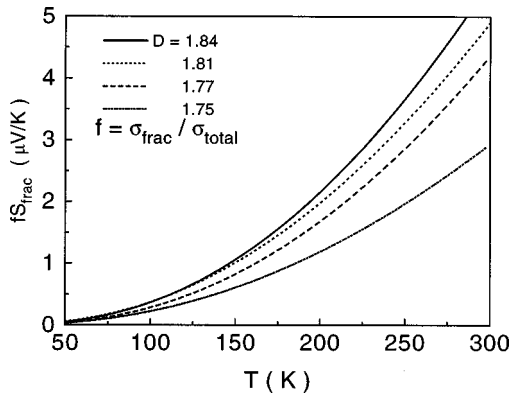

FIG. 4. Temperature dependence of the TEP contributed by the superlocalized carriers on fractals for two groups of the 30/30 and 25/35 nm annealed bilayer films. The data was obtained by subtracting the term AS_0 in Eq. (3).

tals. For the 30/30 nm bilayer films, S_0 in Eq. (3) was replaced by S_0^{a1}, and then fit the experimental TEP data as shown in Fig. 3 (a_2) and (a_3). The optimal constant parameters A, B, T_0, and α are, respectively, shown in Table I. Similarly, for the 25/35 nm bilayer films, S_0 was replaced by S_0^{b1}, and then fit the experimental TEP curves (b_2) and (b_3).

IV. DISCUSSIONS

From the fitting values, α, the superlocalization exponents, $\zeta = D\alpha$, for both groups of the annealed samples are estimated to be 1.35, 1.33 for both 30/30 nm bilayer films with $D = 1.77$ and 1.84, and 1.35, 1.34 for both 25/35 nm bilayer films with $D = 1.75$ and 1.81, respectively. These estimated values for the superlocalization exponent are, to some extent, larger than the theoretical prediction, $1.0 < \zeta < 1.14$, for two-dimensional fractals, but they are surprisingly within the range of 1.14–1.36 for three-dimensional fractals. The calculated values of the activated energy, T_0 are within 650–1100 K for both groups of the bilayer films. In Ref. 6, van der Putten *et al.* obtained an unexpected smaller characteristic hopping energy, $T_0 = 112$ K, between the su perlocalized states on fractals. Our results reported here for T_0 are about 5–9 times larger than theirs. In addition, from Table I, the fitting parameters A and B in each group of the samples are also coherent and comparable, but for different groups of the samples, A is negative for the 30/30 nm bilayer films and positive for the 25/35 nm bilayer films. At present stage, we have no explanations for this difference. By subtracting AS_0 in Eq. (3), the contributions of the superlocalized carriers on fractals to the total TEP are shown in Fig. 4. It is clear that the shape of the curves is very similar to that shown in Fig. 3 (a_2), (a_3) and (b_2), (b_3), and the magnitude is higher than that of the first term in Eq. (3). These results indicate that the total TEP in annealed bilayer films was dominated practically by the carriers superlocalized on fractals, the contributions of the free carriers in Al and the carriers in Ge semiconducting bands to the TEP are relatively small and do not change the main features of the TEP. Therefore, the macroscopic TEP properties for a random system with fractal dimensionality would be significantly determined by some parameters associated with the fractal structures.

It is noteworthy that the above analysis of the TEP data was in terms of the hypothesis that the carriers on fractals are superlocalized, where such an idea was originally proposed for a random percolating fractal system.[3,9,17] In our case, for an Al/a-Ge bilayer film system, the fractal pattern would be, intuitively, more approaching a diffusion-limited aggregation (DLA) fractal, not a random percolation system. However, according to the calculation of the fractal dimension in Al/a-Ge bilayer films, the value of the fractal dimension $D \sim 1.75-1.84$ is higher than 1.7 for two-dimensional (2D) DLA fractals, but smaller than 1.89 for a percolation system.[18]

Although the values we have found for the superlocalization exponent are higher than expected for 2D fractals, we believe that our results qualitatively provide a possible evidence for the superlocalization on fractals in Al/a-Ge bilayer film systems. The difference between the values we obtain experimentally for the fractal dimension D and the fractal dimension of 2D DLA might indicate that our aggregates are, to some extent, different from the ideal 2D DLA fractals. A detailed study on the nature of the fractals in bilayer films would be helpful to further understand the superlocalization in the fractal network. In addition, we also want to point out that the TEP measurements may be a more effective method to investigate the superlocalization in a percolating system than the conductivity. This encourages experimental scientists to study the fractal material macroscopic properties widely and to check the present various theories.

In summary, we investigated the temperature dependence of the resistivity and thermoelectric power (TEP) properties in Al/a-Ge bilayer film systems with fractal structures. The results showed that the TEP properties are closely associated with the fractal structures. By analysis of the data, we provide possible evidence for the superlocalization of the carriers on fractals in such bilayer film systems, and the estimated superlocalization exponents are within $1.33 < \zeta < 1.35$.

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