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Thermoelectric Properties of AlPdRe Quasicrystalline Thin Films

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Icosahedral quasicrystalline thin films of AlPdRe system with thickness of 108~210 nm were prepared by a molecular beam epitaxy method and post-annealing. Thermoelectric properties of the films have been measured. A 3ω method has been utilized for the measurement of thermal conductivity of quasicrystalline thin films. We report the enhancement of dimensionless figure of merit in thin films by a factor of two in compared to the bulk quasicrystals. The origin of the enhancement of thermoelectric performance will be discussed based on the structure of thin films and the electronic structure near Fermi energy, that is, the density of states pseudogap.

Key words: icosahedral quasicrystal, thin film, MBE, pseudogap, 3-omega method

1. INTRODUCTION

Icosahedral quasicrystal (IQC) has a unique atomic structure, which can be distinguished from crystal or amorphous solid. The structure is characterized by the sharp diffraction peaks with an icosahedral rotational symmetry in reciprocal space, and the quasi-periodic packing of icosahedral atom clusters. Unlike conventional metallic alloys, many IQC's possess a semiconductor-like electron transport behavior [1] and a glass-like low thermal conductivity [2]. These properties can be explained by the combination of a Hume-Rothery type pseudogap in the electron density of states (DOS) at Fermi energy (E_F) and a localization tendency of electrons and phonons. We reported that AlPdRe IQC possesses higher thermoelectric power and lower thermal conductivity than other IQC's and thus might be candidate for a thermoelectric material [3]. It was shown that the thermoelectric power of AlPdRe IQC sensitively increases with increasing transition metal (TM: Re or Pd) concentration. The slight change in the concentration of Pd and Re is supposed to cause the formation of covalent bonds in Al-TM icosahedral clusters and the significant variation in the DOS pseudogap [3][4]. Hence, further precise tuning of the sample composition and flexible control of the forth element doping are necessary for the improvement of the thermoelectric performance. However, the previous study based on the bulk samples showed some difficulties in the control of the sample composition and the porosity [3]. Thin films preparation is expected less porosity and thus more reliable researches of the thermoelectric property in comparison with the bulk samples. Some researchers reported the preparation and electrical properties of AlPdRe IQC thin films [5][6]. However, their purposes were mainly the examination of electron localization at very low temperature based on a quantum interference theory. The thermoelectric performance of IQC thin film above room temperature, measuring all of the thermoelectric power, electrical conductivity, and thermal conductivity for the same film has not been investigated yet. The preparation of high quality thin film of IQC is a start point of more complex structure such as nm-order multi-layer of IQC, in which structural modifications of a quasi-lattice or icosahedral atom clusters provide a new DOS pseudogap structure and enhance the thermoelectric performance.

In this paper, we report the results of preparation and thermoelectric property measurements of the single phase of AlPdRe IQC thin films. The dimensionless figure of merit is estimated. Finally, the possibility of the IQC as a thermoelectric material is discussed.

2. EXPERIMENTAL PROCEDURE

The thin films of AlPdRe IQC were prepared using a molecular beam epitaxy (MBE) apparatus. The details of our film deposition procedure was described elsewhere [7]. The simultaneous depositions of Al, Pd, and Re were performed at substrate temperature of 30 ~ 90 ℃. The pressure during deposition was 10^{-6}~10^{-5} Pa. The deposition rates were 0.6~1.2 nm/min, 0.12~0.30 nm/min, and 0.06~0.18 nm/min for Al, Pd, and Re, respectively. These deposition rates are lower than those previously reported [6][8]. The desired composition was $Al_{70}Pd_{20}Re_{10}$ for all of the films. Sapphire R-plane was employed as a substrate. In order to check the oxidation of the as-deposited films, we used *in situ* X-ray photoelectron spectroscopy (XPS). The deposited films were taken out from the MBE chamber and then annealed under Ar atmosphere (6N purity, flow rate of more than 500 cm^3/min) at 700~750 ℃ up to 2 hours. X-ray diffraction (XRD) patterns were measured to identify the alloy phase. The surface morphology of the films was examined by a field-emission-type scanning electron microscope (FE-SEM). Thickness of the films

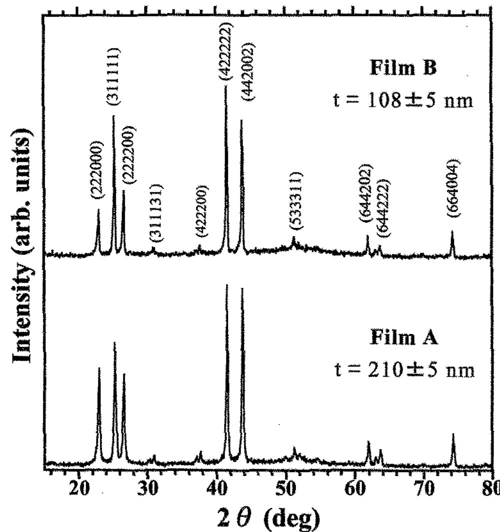

Fig. 1 XRD patterns of the AlPdRe IQC thin film samples, A and B. Numbers in the parentheses are six-dimensional indices. Thickness of the film, *t*, is also described on each XRD patterns.

was measured by a stylus-type thickness meter and a FE-SEM sectional micrograph.

Before all of the measurements below, the Ar+ sputtering of surface oxidized layer was performed. The thermoelectric power, *S*, and the electrical conductivity, σ, were measured in pure He atmosphere in the temperature range from 350 to 700 K, by the steady-state temperature gradient method and the dc four-probe method, respectively. The maximum temperature difference was approximately 7 K. Thermal conductivity, κ, was measured using the thin film 3ω method. Cahill *et al.* described a detailed explanation for the measurement [9]. Before the 3ω measurement, thin film alumina (Al_2O_3) with a thickness of 360 nm was deposited on the IQC film for the electrical insulation between metal line and IQC film. Recently, the similar measurement has been performed for the thermoelectric superlattices such as Bi_2Te_3/Sb_2Te_3 [10].

3. RESULTS AND DISCUSSION

3.1 Sample characterization

The XRD patterns of the film A and B after deposition and annealing are shown in Fig. 1. Single phase of the IQC was obtained by annealing the as-deposited film of amorphous phase. All of the sharp diffraction peaks can be indexed by six dimensional indices. The XRD patterns are similar to the powder patterns (for instance, JCPDS No.45-1317). The sharp diffraction peaks are similar to those of the bulk samples [3]. The diffraction intensities of five-fold direction such as (311111) plane and (422222) plane are relatively intense in comparison with other diffraction peaks. We consider, however, no strong preferred orientation judged from the XRD total pattern profile. Figure 2 shows the FE-SEM micrographs of the IQC film C after the Ar+ sputtering of the surface oxide layer. We also observed that all the film surfaces are entirely smooth

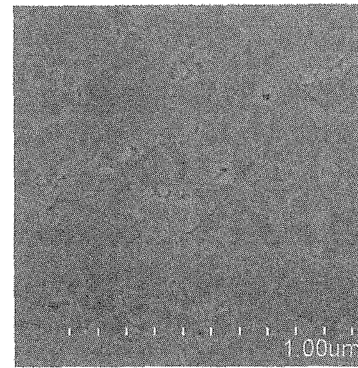

Fig. 2 FE-SEM micrograph of film B.

more than μm order area. It should be noted that we have obtained more smooth IQC film than the previous studies [5][6][8]. Moreover, the film C consists of the very small grains with a diameter of several tens of nanometers. This diameter is several tens times smaller than that of bulk sample.

3.2 Electrical properties

Figure 3 shows the temperature dependence of *S* of the IQC films. The data of the bulk IQC samples (Bulk1: $Al_{67.8}Pd_{22.2}Re_{10.0}$, Bulk2: $Al_{67.7}Pd_{23.2}Re_{9.1}$, and Bulk3: $Al_{68.5}Pd_{22.9}Re_{8.6}$, from Ref. [3]) are also shown for comparison. Although the same composition was designed for films A and B, the thermoelectric power S exhibits different values. It seems that the thinner the film thickness, the larger the value of *S*. However, we could not determine the thickness dependence of *S* because the IQC thin films in this work consist of poly grains and the preferred orientation is not clearly observed. This result suggests that the *S* is sensitive to the alloy composition. In the case of bulk samples, the value of *S* rapidly increases with increasing slightly the TM concentration and the polarity change from negative to positive was observed at higher temperature for TM-poor samples [3]. These characteristics were also previously reported in other Al-based IQC and can be understood by taking the DOS pseudogap into account. We will give the qualitative interpretations about the S behaviors for the thin films based on the pseudogap later.

The temperature dependence of σ of the IQC films is shown in Figure 4. Apparently, the σ values are much larger than those of the bulk IQC. In addition, the σ monotonically increases with increasing temperature. In many IQC alloys, power law temperature dependence, $\sigma \sim T^p$, was observed [1]. For our IQC thin films, we get $p \sim 2$ for all the films by a least square fitting. This value is similar to that of the bulk samples of AlPdRe IQC [11]. Therefore, the effect of a metallic secondary phase, which is particularly serious for the thin films, can be ignored. The semiconductor-like positive temperature coefficients of σ are explained by a delocalization effect of localized electrons by inelastic scattering and the inter-band transition occurring between the spiky DOS's in the pseudogap. The values of σ are 2 ~ 4 times larger than those of bulk samples. This fact can be

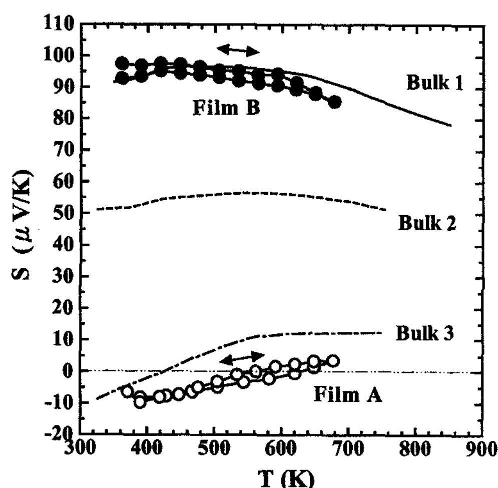

Fig. 3 Temperature dependence of the thermoelectric power. Data of the bulk samples are also plotted. The compositions of the bulk samples are described in the text.

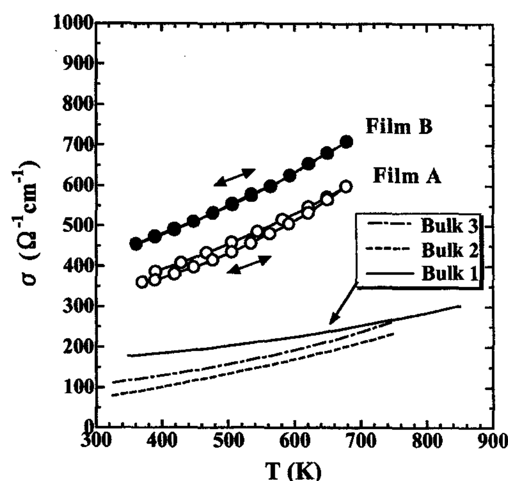

Fig. 4 Temperature dependence of the electrical conductivity. Data of the bulk samples are also plotted.

attributed to the less porosity in comparison with the bulk. Moreover, we have to consider that the film compositions might be slightly different from our previously investigated bulk samples [3].

These sample dependences of S and σ can be qualitatively understood by not only the dense structure but also the composition dependence. The XPS spectrum of the surface oxidized layer, which was formed by annealing, exhibited mainly the peaks of aluminum and oxygen. Therefore, the composition of the film shifts from that of the as-deposited film to some extent. The determination of film compositions using chemical analysis is in progress. According to the analogy of composition dependence of S for the bulk samples shown in Figure 3, the film B are supposed to have higher TM concentrations than the film A. The slight

Table I
Thermal resistance, R, and thermal conductivity, κ, of IQC thin films at room temperature. The thermal resistance of alumina cover-layer (thickness of 360 nm), R_a, is $3.33\pm0.01\times10^{-7}$ m^{2}K/W. $\kappa = t / (R - R_a)$, where t is a film thickness. κ_{ph} is a phonon thermal conductivity.

	R $\times10^{-7}$ [m^{2}K/W]	$R-R_a$ $\times10^{-7}$ [m^{2}K/W]	κ [W/mK]	κ_{ph} [W/mK]
Film A	4.74 ($\pm$0.30)	1.41 ($\pm$0.31)	1.56 ($\pm$0.23)	1.26 ($\pm$0.23)
Film B	4.58 ($\pm$0.50)	1.25 ($\pm$0.51)	1.03 ($\pm$0.40)	0.66 ($\pm$0.40)
Bulk 1	–	–	0.66 ($\pm$0.07)	0.57 ($\pm$0.07)
Bulk 2	–	–	0.79 ($\pm$0.08)	0.75 ($\pm$0.08)
Bulk 3	–	–	0.99 ($\pm$0.10)	0.90 ($\pm$0.10)

increase in the TM concentration causes a deepening of the DOS pseudogap and a shift of E_F as we examined the covalent bonding nature of Al-TM icosahedral clusters by an atomic density measurement [4] and a X-ray charge density study [12]. Consequently, for the case of film B, the change in the DOS pseudogap structure may increase σ and maintain S with increasing the TM concentration. More quantitative discussion using a result of two-band-model fitting will be given in the future.

3.3 Thermal Conductivity

From the measurement of a 3ω method we could obtain a thermal resistance, R (= t/κ), of each film, where t is a film thickness. The room temperature thermal resistance and thermal conductivity data are summarized in Table I. Since alumina cover-layer was deposited on the IQC film, its thermal resistance should also be taken into account. The thermal resistance of the alumina layer was subtracted by measuring that of the reference sample, in which the alumina layer was solely deposited on the sapphire substrate. In sub-micron order thin film, we should also take care of the thermal resistance of solid-solid interface such as film/substrate or film/cover-layer. According to recent reports on nano-scale thermal transport and interface thermal resistance [13], values of thermal resistance of the solid-solid interface are known to fall into the range of 2×10^{-10} ~ 2×10^{-8} m^{2}K/W for various materials. These values are less than 1/10 of the total thermal resistance of our films and negligible. Both IQC films A and B seem to possess similar thermal conductivity to the bulk samples [3]; nevertheless those films have less porosity and dense structure. The phonon thermal conductivity, κ_{ph}, was estimated by subtracting an electron contribution, κ_e, from the total thermal conductivity using Wiedemann-Franz law. The value of κ_{ph} of film B is comparable to the minimum thermal conductivity, κ_{min} (~ 0.7 W/mK), which is derived when the phonon mean free path is equal to half of the phonon wavelength. We

suggest that the fine grains in the IQC film give rise to the intense grain boundary scattering of phonons and significantly reduce the κ_{ph}.

3.4 Thermoelectric Performance

The dimensionless figure of merit, *ZT*, of the film B was estimated. We assumed that at higher temperature than room temperature, κ_{ph} exhibit constant value and κ is sum of κ_{ph} and κ_e, which is estimated using Wiedemann-Franz law. As a result, it was found that the *ZT* of the film B reaches maximum value of approximately 0.2 at 600 K. This maximum value is two times larger than that of our previously investigated bulk samples. The enhancement of *ZT* is caused by the improvement of the structure (dense and fine poly grains) and the film composition as mentioned above.

The enhancement of *ZT* presented here is not special for the thin film. The similar enhancement can be expected for bulk IQC's if we improve the bulk preparation process, for example, the sintering to obtain the dense and fine poly grains, and the precise tuning of composition.

4. CONCLUSION

The AlPdRe icosahedral quasicrystalline thin films with thickness of 108~210 nm were prepared by a molecular beam epitaxy method and post-annealing. The films consist of dense and fine poly grains with a diameter of several tens of nanometers and do not exhibit strong preferred orientations. The most remarkable feature is that the absolute value of electrical conductivity is several times larger than that of bulk samples. The thermoelectric power and thermal conductivity of thin films are comparable to those of bulk samples. The dimensionless figure of merit of the quasicrystalline thin film seems to reach maximum value of approximately 0.2 at 600 K. This maximum value is two times larger than that of bulk quasicrystal among all of our previously investigated samples. The enhancement of *ZT* is caused by the improvement of the structure (dense and fine poly grains) and the film composition.

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