

Abnormal magnetoresistance effect in self-doped $\text{Ag}_{2+\delta}\text{Te}$ thin films ($\delta \leq 0.25$)

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We report an abnormal room-temperature magnetoresistance behavior in self-doped $\text{Ag}_{2+\delta}\text{Te}$ films with Ag doping concentration $\delta \leq 0.25$. Both positive magnetoresistance and negative magnetoresistance are found with the magnetic field applied along perpendicular to the sample surface and opposite direction, respectively. It is also evident from our study that such magnetoresistance (MR) behavior is strongly dependent on the doping concentration δ and the annealing time. The origin of the MR behavior is discussed and tentatively ascribed to the complex structure of the films, which is analyzed by x-ray measurement.

Recently, there has been growing interest in the nonmagnetic compounds such as silver chalcogenides due to their large magnetoresistance (MR) effect.^{1,2} Xu *et al.*¹ reported that the self-doped silver chalcogenides, $\text{Ag}_{2+\delta}\text{Te}$ and $\text{Ag}_{2+\delta}\text{Se}$ ($\delta \approx 0.01 \sim 0.33$), possess a large MR ratio, $\Delta\rho/\rho$, up to 400% at 4.5 K and 60 kOe (120% at room temperature and 40 kOe). Later, large MR ratio of 300% at 50 K and 70 kOe (60% at room temperature and 50 kOe) was also observed in $\text{Ag}_{1.73}\text{Te}$ thin films by Chuprakov and Dahmen.² The temperature dependence of the MR of the films is different from that of the bulk material.¹ Although it was already proposed to be related with the carrier density, microstructure and other physical factors in the samples, however, the mechanism of the MR of self-doped silver chalcogenides is still not clear now.

In this paper, we report an abnormal MR behavior in Ag self-doping $\text{Ag}_{2+\delta}\text{Te}$ films. Both positive magnetoresistance (MR-*p*) and negative magnetoresistance (MR-*n*) are obtained with the magnetic field applied along two opposite directions, $+z$ and $-z$ axis. Here z axis is defined as the field direction perpendicular to the film surface and the magnetic field H applied along $+z$ and $-z$ directions correspond to positive magnetic field ($+H$) and negative magnetic field ($-H$) during the MR measurements, respectively. Such abnormal MR behavior occurs only when $\delta \leq 0.25$ in the $\text{Ag}_{2+\delta}\text{Te}$ films annealed at 430 °C for 3 h. If the annealing time $t > 3$ h or $\delta > 0.3$, only MR-*p* is observed. The possible origin of the MR behavior is also discussed.

Ag-Te multilayers were prepared on $22 \times 22 \text{ mm}^2$ glass substrates by using electron-beam evaporation with the base pressure better than 10^{-6} Torr in the chamber. The evaporation rate of Ag and Te was about 0.5 Å/s, which was controlled by a quartz crystal monitor. The structure of the films was: substrate/Ag(400 Å)/Te(500 Å)/Ag(d_{Ag})/Te(200 Å)/Ag(200 Å), where different values of the Ag thickness d_{Ag} were used for different samples in order to vary the Ag doping concentration δ in the $\text{Ag}_{2+\delta}\text{Te}$ thin films. The as-deposited films were annealed *in situ* at about 10^{-6} Torr for alloying. The Ag doping concentration δ was first selected by calculating stoichiometry for the films and further examined by an inductively coupled plasma-atomic emission spectrometer³ (Thermo Jarrell-Ash Corp., IRIS/AP) after the

films were prepared. In our experiments the doping concentration δ was 0.2, 0.25, 0.3, 0.4, and 0.5. Crystal structure of the films was examined by x-ray diffractometer. The room-temperature MR was measured with the standard dc four probe method in an applied magnetic field normal to the film plane. The field varied between 20 and -20 kOe. The current was applied in the film plane and small enough in order to eliminate self-heating effect. The measurements were performed with a current $I = 100 \mu\text{A}$.

The MR ratio $\Delta\rho/\rho$ as a function of the magnetic field H for the different doping concentration δ in the $\text{Ag}_{2+\delta}\text{Te}$ films is shown in Fig. 1. All the film samples were annealed at 430 °C for 3 h. The MR ratio here is defined as $\Delta\rho/\rho(0)$ [$\Delta\rho = \rho(\pm H) - \rho(0)$]. The most interesting MR behavior as one can see from Fig. 1 can be described as follows: the MR behavior is strongly dependent on the doping concentration δ . For $\delta = 0.4$ and 0.5, only MR-*p* is found with the field applied in both $+z$ and $-z$ directions and the MR-*p* ratio

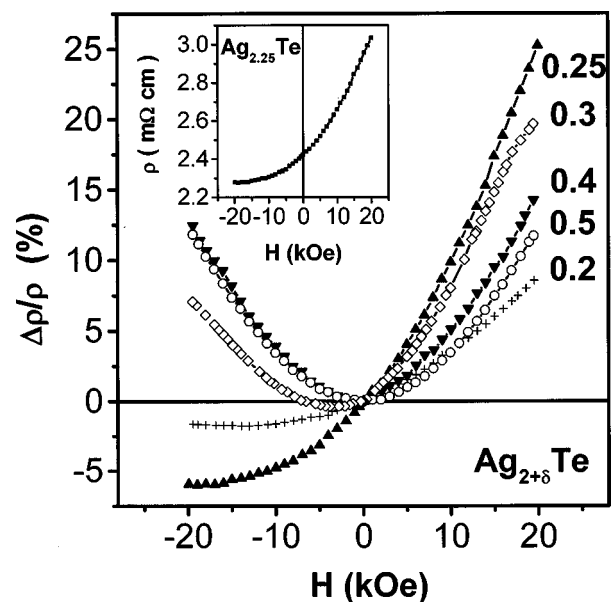


FIG. 1. MR of $\text{Ag}_{2+\delta}\text{Te}$ films as a function of magnetic field H for different δ . The inset shows resistivity ρ of the $\text{Ag}_{2.25}\text{Te}$ film as a function of magnetic field H . All the samples were annealed at 430 °C for 3 h.

$\Delta\rho/\rho$ vs $\pm H$ is symmetric. However, when $\delta=0.2$ and 0.25 , MR- p is observed in field applied along $+z$ direction, while, surprisingly, MR- n , i.e., $\Delta\rho/\rho < 0$, is found in field applied along $-z$ direction. Moreover, in case of $\delta=0.3$, a transition from MR- n to MR- p can be seen clearly at $H = -6$ kOe. Thus the MR is positive and symmetric in heavily doping concentration δ , while the MR is negative in lightly doping concentration δ . Transition from MR- n to MR- p can also occur in mediate doping concentration. Obviously, such complex MR behavior in field applied along $-z$ direction is dependent on the Ag doping concentration δ in the $\text{Ag}_{2+\delta}\text{Te}$ films.

During MR measurements, two processes are used. One is that the MR was measured with the field increased from 0 to 20 kOe, then decreased to the -20 kOe and again increased to 0. The other is that the MR was measured with field started from 20 kOe to 0, then decreased from 0 to -20 kOe. Both processes give the same MR results due to the fact that the nonmagnetic $\text{Ag}_{2+\delta}\text{Te}$ films do not have any magnetic hysteresis effect. In addition, MR behavior is not affected by changing the direction of the measuring current in the films. Moreover, attention has also been paid to the current strength effect on the MR behavior. We note that if the current changes within some extent, one can still obtain the same MR behavior for all the films.

We also note that the MR- n behavior found in our samples is different from that in previous studies in other materials.⁴⁻⁶ The MR of our samples shows clear dependence on the directions of applied field. For lightly doping samples, the MR- n is only found in field applied along $-z$ direction, while the MR- p is observed in field applied along $+z$ direction, exhibiting an asymmetry behavior. However, in other studies, longitudinal and transverse MR show no dependence on the directions of applied field, such as in $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films⁴ and granular Ag-Ni alloys,⁵ in which one can obtain the same MR behaviors in field applied along $+z$ or $-z$ direction. Another remarkable difference is that our MR- n is obtained at room temperature, while in other cases, the MR- n is normally observed at very low temperature.

The picture of the MR of such systems is rather complicated and diverse depending on numerical physical factors. As we know, although MR- p can be explained by the classical model considering the effects of the Lorentz force⁷ on the carriers moving in a crystal, it is difficult to explain the MR results in both film and bulk silver telluride. Recently, the natural multilayer model,² assuming one period includes two Ag-Te and one Ag layers, has been proposed to explain the observed MR- p phenomenon in Ag-Te films. Another important model by Shklovskii⁸ has received considerable attention. He suggests that the contraction of the electron wave function in magnetic field is mainly responsible for the MR- p . On the other hand, MR- n has also been observed in various kinds of doped semiconductors. According to Toyozawa,⁹ the conduction electrons are scattered by localized magnetic moments of impurities. Thus the applied magnetic field orders these magnetic moments and reduces the scattering effects, which causes the decrease of resistivity and leads to the MR- n . Yazawa¹⁰ also proposed that with increase magnetic field, the density of states and carrier density increase, resulting in the MR- n .

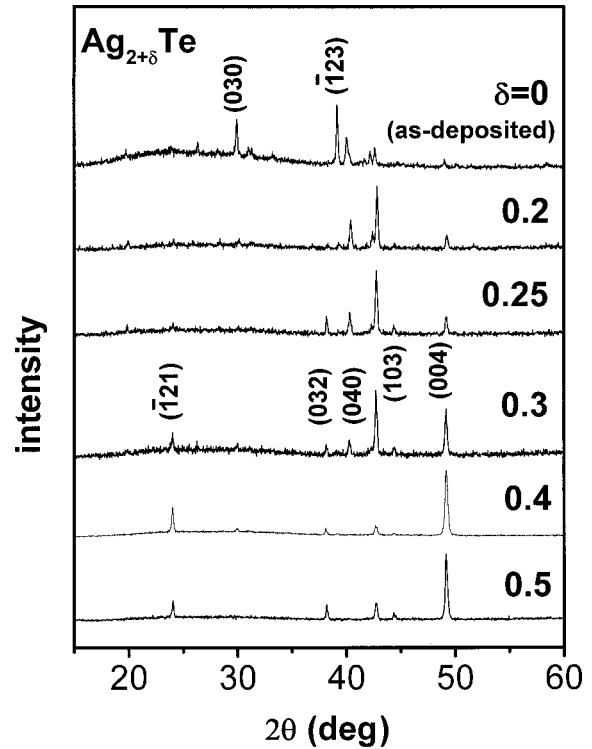


FIG. 2. The x-ray-diffraction patterns of the as-deposited Ag_2Te film and the $\text{Ag}_{2+\delta}\text{Te}$ films with different δ annealed at 430°C for 3 h.

However, these models can only explain either the MR- p or the MR- n , but seem incapable of explaining the coexistence of both MR- p and MR- n in $\text{Ag}_{2.2}\text{Te}$ and $\text{Ag}_{2.25}\text{Te}$ films as shown in Fig. 1.

It is generally found that the MR- p shows H^2 dependence in low field and linear dependence on H in high field for some semiconductors. Through analyzing the relationship between the MR and magnetic field, we also find that MR- p exhibits H^2 dependence. In our samples, the MR- p does not saturate up to $H=20$ kOe due to intrinsic property of $\text{Ag}_{2+\delta}\text{Te}$. Similar results are also observed in the bulk¹ $\text{Ag}_{2+\delta}\text{Te}$ for $0.01 \leq \delta \leq 0.33$ and in the $\text{Ag}_{1.73}\text{Te}$ films.² As shown in Fig. 1, both maxima of MR- p and MR- n are about 25 and -6% found in $\delta=0.25$ at 20 and -20 kOe, respectively. The inset of Fig. 1 shows an abnormal room-temperature resistivity ρ as a function of the magnetic field H for $\text{Ag}_{2.25}\text{Te}$ film. The ρ of $\text{Ag}_{2.25}\text{Te}$ film at zero field is about 2.43 m Ω cm which is in agreement with the data of bulk and films of silver telluride^{1,2} at room temperature.

To further understand the MR behavior in our system, we also examined the structure of our films by x-ray analysis. In Fig. 2, we present the x-ray-diffraction (XRD) patterns of the as-deposited Ag_2Te film and the $\text{Ag}_{2+\delta}\text{Te}$ films annealed at 430°C for 3 h.

Previous studies found that the extra silver atoms in $\text{Ag}_{2+\delta}\text{Te}$ material can occupy the tetrahedral, octahedral, and triangular interstices.^{11,12} The appearance of the peaks of monoclinic phase of Ag_2Te film^{2,13} is also found quite different from that of bulk Ag_2Te ^{13,14} that the (004) peak for the film is much stronger than that expected for the powder sample. And a strong ($\bar{1}21$) texture was also seen in Ag-Te

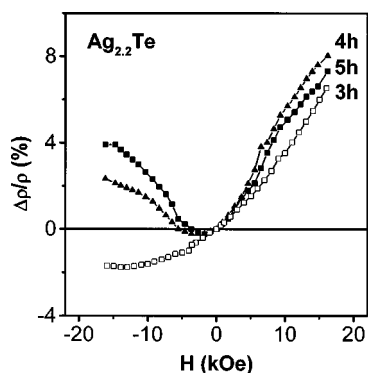


FIG. 3. MR of the $\text{Ag}_{2.2}\text{Te}$ films as a function of magnetic field H for different annealing time at 430°C .

films. In our study, we found that the peaks for the Ag-Te films can be indexed with monoclinic phase of Ag_2Te . However, there is a strong (004) peak of monoclinic phase in our films, which indicates a strong (004) texture. The striking phenomenon is that the relative intensity of (004) peak, or the texture, of $\text{Ag}_{2+\delta}\text{Te}$ films is strongly dependent on the doping content δ . As shown in Fig. 2, the peaks of (004) and ($\bar{1}21$) are nearly invisible in the doping-free film. However, as increasing the doping concentration δ , the peak of (103) is pronounced as $\delta=0.2$ and 0.25 , and it decreases while the (004) peak increases with increasing the δ .

It was found that the orientation of Ag-Te films might have strong effect on the MR behavior that it exhibits different temperature dependence for oriented and nonoriented films.^{2,15,16} Our studies may also imply a relationship between the structure and the MR behavior for the Ag-Te films. From the analysis of the structure and MR behavior, we can see that the appearance of MR- p might associate with (004) peak, while the appearance of MR- n might associate with the existence of (103) peak. So there might be a relationship between the texture, or the (004) or (103) peaks, and the MR- p or MR- n in our samples, however, it is not a simple linear dependence relation, which can be seen in Figs. 1 and 2. Therefore we tentatively believe that the origin of the MR behavior might be ascribed to the texture of the films. However, more detailed studies, especially on the microstructures of the films, are needed for further understanding of the MR behavior.

We further present studies of the annealing effect on the structure and the MR behavior of our samples. Figure 3 shows MR ratio, $\Delta\rho/\rho$ as a function of applied field H for

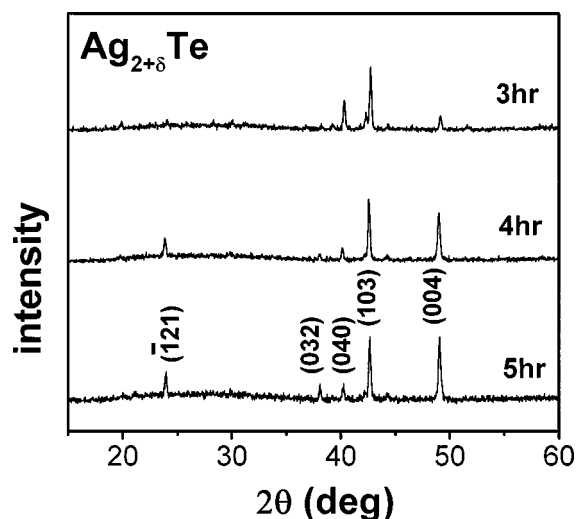


FIG. 4. The x-ray-diffraction patterns of the $\text{Ag}_{2.2}\text{Te}$ films annealing at 430°C for 3, 4, and 5 h.

the $\text{Ag}_{2.2}\text{Te}$ films annealed at 430°C with different annealing time. As one can find that the annealing time strongly affects the sign and magnitude of the MR. When annealing time is over 3 h, the MR- n behavior disappears and only the MR- p is found in field applied along $-z$ direction. Such annealing effect appears in all the samples. In addition, the MR of those annealing films is larger than that of the as-deposited $\text{Ag}_{2.2}\text{Te}$ film.

X-ray analyses for these films are also presented in Fig. 4. It is evident that annealed films exhibit a tendency for (103) and (004) orientation with increasing annealing time. One can also note that the annealing time strongly affects the intensity of (004) peaks and it increases with increasing the annealing time, while the intensity of (103) peak changes slightly when the time is over 3 h.

In conclusion, the abnormal transverse MR behavior is observed in self-doped $\text{Ag}_{2+\delta}\text{Te}$ films. We observe both MR- p and MR- n in Ag doping concentration $\delta \leq 0.25$ with the field applied along in opposite directions normal to the film plane. It is also evident from our study that such MR behavior is strongly dependent on the doping concentration δ and the annealing time. The abnormal MR behavior is discussed and tentatively ascribed to the complex structure of the films, which is analyzed by x-ray measurement.

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