Hall effect in Al–W thin films

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Abstract

The Hall coefficient, $R_H$, electrical resistivity, $\rho$, and temperature coefficient of resistivity, $\alpha$, of $\text{Al}_x\text{W}_{100-x}$ ($61 \leq x \leq 88$) thin films and amorphous-like tungsten films are reported. The $\text{Al}_x\text{W}_{100-x}$ films have been prepared by magnetron co-deposition of pure metals onto glass substrate. Films are X-ray amorphous for $63 \leq x \leq 86$. Amorphous-like tungsten films ($x = 0$) were obtained at sputtering conditions different from those applied for the preparation of Al–W alloys. The $R_H$ value is strongly dependent upon the alloy composition: it changes sign from positive to negative at $x < 78$, and exhibits a maximum for $x < 68$ at.%. With the decrease of Al content, $\rho$ steeply increases and exhibits a maximum at $x \approx 80$ at.%. The temperature coefficient of the resistivity exhibits large negative values, with a well-defined minimum at $x < 80$. The Hall coefficient of films with $67 \leq x \leq 80$ has also been determined at liquid nitrogen temperature, and the values obtained were the same as the room temperature values. Since the value of electrical resistivity of the examined alloys in the temperature interval from 77 to 300 K noticeably changes (10%), a significant anomalous contribution to the Hall effect is thus excluded.

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1. Introduction

One of the most interesting properties of the non-magnetic amorphous alloys is the occurrence of a positive Hall coefficient $R_H$, that is contrary to predictions of the free-electron model. As a rule, a positive $R_H$ occurs in the alloys of early transition (TE) and late transition (TL) metals, when the composition is dominated by TE component [1]. There are two (not mutually exclusive) explanations for the occurrence of positive $R_H$ in these alloys. According to the first approach, the Hall effect in disordered TE–TL alloys is inferred either through the S-shaped dispersion curve [1,2] or by the minimum in the electronic density of states [3], which are both due to the strong electron scattering and the strong s–d hybridization.

According to the second approach [4,5], there is, even in non-ferromagnetic transition-metal (TM) alloys, a strong magnetic contribution to $R_H$. This contribution is due to the high resistivity of these alloys and to the effects of strong spin–orbit interaction of the d-band conducting electrons. Recently, it has been argued that even in the Ca–Al(Au) alloys, a complete description of the Hall effect must incorporate both the effects of s–d hybridization and spin–orbit interaction [6,7].

Beside the extensive investigation of the true TE–TL amorphous alloys, there is also a considerable interest in the corresponding ternary [8–11] systems, which contain aluminum as a component. As for binary Al–TM alloys, the measurements are reported for the Al–V [12] and Al–Ti [13] alloys. In the Al–TM alloys, the Hall coefficient $R_H$, the resistivity $\rho$ and the temperature coefficient of resistivity at room temperature $\alpha = (d\rho/dT)/\rho$, are all strongly dependent on aluminum concentration. The Hall coefficient is found to be negative if the amorphous alloy is rich enough

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in aluminum [8,13]. On the TM-rich side, the $R_H$ is positive for TE-rich alloy and may be negative for TL-rich alloys [8]. As a rule, it can be taken that in the Al–TM amorphous alloys (except for the alloys with Al content somewhat greater than 80 at.%) the addition of aluminum shifts: $R_H$ to higher positive values, $\alpha$ to higher negative values, and resistivity to higher values. The shift of $R_H$ is usually attributed to the strong effects of spin–orbit interaction and high resistivity of these alloys [10,13].

Here we present the results of measurements of the Hall effect, electrical resistivity, and temperature coefficient $\alpha$ in Al$_x$W$_{100-x}$, thin films with $x = 0$ (pure tungsten) and $61 \leq x \leq 88$ prepared by magnetron sputtering. The obtained films are X-ray amorphous for $63 \leq x \leq 86$. Amorphous-like tungsten films ($x = 0$) were obtained at different sputtering conditions than those applied for preparation of Al–W alloys. The Hall resistivity of five films with $67 \leq x \leq 80$ has been measured both at liquid nitrogen and room temperature (LNT and RT, respectively). The results obtained are discussed with respect to the occurrence of anomalous Hall effect.

2. Experimental

The Al$_x$W$_{100-x}$ thin films were prepared by a simultaneous d.c. sputtering of both pure components in a two source sputtering apparatus described elsewhere [14]. The sputtered Al and W atoms were deposited onto glass substrates of a disk shape, with 1 cm in diameter and 0.3 mm thick, and held at room temperature. Argon was used as a working gas at 0.7 Pa pressure and in a continuous flow, and the film deposition rate was about 0.3–0.4 nm/s. In order to ensure the lateral homogeneity of the deposited films, the substrate holder rotated during the deposition. The macroscopic lateral homogeneity of the films was checked by the measurements of temperature variation of the resistivity with different positions of the current and voltage contacts. The same value of coefficient $\alpha$ for different geometries indicated the absence of compositional gradient along the film. The composition of the alloys was determined from the measurements of the deposition rates of pure components, and checked by proton induced X-ray emission (PIXE) on several samples. The estimated uncertainty of the film composition is about 10% relative to the minor component. The amorphous-like tungsten films were prepared by magnetron sputtering of both pure tungsten cathodes at working gas pressure of about 3 Pa. The amorphous-like nature of such tungsten films is due to the incorporation of about 12–19 at.% of chemically unbound oxygen into the film [15].

The thickness of the Al$_x$W$_{100-x}$ films was measured with a profilometer, and was in the 1.4–2.1 $\mu$m range, while the thickness of the amorphous tungsten films was measured by the SEM observation at the fractured samples, and was about 200 nm. The uncertainty in thickness was about 5%.

The structure of the films has been determined by X-ray diffraction, using a Philips PW 1820 vertical goniometer with mono-chromatized Cu K$_\alpha$-radiation. Completely amorphous films were prepared in the composition range from Al$_{63}$W$_{37}$ to Al$_{86}$W$_{14}$, while the films for $x = 61$ and 88, respectively, contained the traces of crystalline phases (Fig. 1).

The Hall effect measurements were performed by the five-point method and by a standard ac technique in magnetic fields up to 1 T. In order to minimize the influence of the electrical contacts, triangular silver flakes have been evaporated onto the substrate before the Al–W film deposition, and only a small pointed part (about 0.2 $\times$ 0.2 (mm) of the flakes overlapped with the film. The 50 $\mu$m Cu wires were mounted with the silver paint onto the outer parts of the flakes. In case of pure tungsten, Cu wires were mounted with the silver paint directly onto the films. The silver paint contacts are the largest source of noise in our measurements. The current through the samples was in
the range from 5 to 15 mA for Al–W films and 1 mA for pure tungsten films. The uncertainty in $R_H$ values originating from the measurement noise was about $0.1 \times 10^{-11}$ m$^3$ C$^{-1}$.

3. Results

The values of $R_H$, $\rho$ and $\alpha$ at room temperature for the Al$_x$W$_{100-x}$ thin films are given in Table 1. Two values for amorphous-like tungsten indicate the upper and lower limits of typically observed values. The Hall coefficient $R_H$ as a function of Al content is shown in Fig. 2. We have included also the results for $R_H$ in amorphous Cu–W thin films [16] and the values for liquid [17] Al and Cu. The values of $R_H$ for $67 \leq x \leq 80$ were determined at liquid nitrogen temperature as well. These alloys were selected because they exhibit a large negative $\alpha$ and/or the $R_H$ values which deviate significantly from the expected free-electron values. However, the observed values of $R_H$ at LNT were the same (within the experimental error of about $0.1 \times 10^{-11}$ m$^3$ C$^{-1}$) as those obtained at room temperature. We expect that the same holds for the other amorphous Al–W alloys examined, as well.

We note that in the amorphous Al–W films, $R_H$ exhibits a similar dependence on Al concentration as in other Al–TM amorphous alloys [8,9,13]. On Al-rich side, the $R_H$ of amorphous alloys extrapolates to the higher negative [8] values than that measured for liquid aluminum. On the other side, with the decrease of Al content, the $R_H$ steeply increases and becomes positive for $x \approx 78$ at.%. With further decrease of Al content, the $R_H$ exhibits a broad maximum at $x \approx 70$ at.%. A similar maximum was observed in amorphous Ti–Al [13], (TiNi)-Al [8,9] and (NiZr)-Al [8] alloys. The comparison with the results for Cu–W alloys confirms a general observation that in the alloys which contain Al, $R_H$ is more strongly dependent on the alloy composition than in other TM based alloys.

The dependence of electrical resistivity and temperature coefficient $\alpha$, at room temperature, on the Al–W alloy composition is shown in Fig. 3. The scattering of the obtained values for the resistivity is apparently due to the accumulation of errors in determination of geometrical factors, which are mutually cancelled in derivation of the temperature coefficient $\alpha$. Nevertheless, it is seen that with the addition of tungsten, $\rho$ steeply increases and exhibits a maximum at about 20 at.% of tungsten.

The temperature coefficient of resistivity, $\alpha$, of the Al$_x$W$_{100-x}$ thin films at room temperature exhibits large negative values, with a well defined minimum for $x = 80$.

![Fig. 2. The Hall coefficient of the Al$_x$W$_{100-x}$ thin films and Cu$_x$W$_{100-x}$ amorphous alloys, as a function of aluminum and copper content, respectively. The values for liquid Al and Cu are given by H.U. Kinzi and H.-J. Guntherodt [16], and the values for Cu–W amorphous alloys are determined by Ivkov et al. [15].](image)

Table 1

<table>
<thead>
<tr>
<th>x (at.%)</th>
<th>$R_H$ (300 K) ($10^{-11}$ m$^3$ C$^{-1}$)</th>
<th>$R_H$ (77 K) ($10^{-11}$ m$^3$ C$^{-1}$)</th>
<th>$\rho$ (300 K) ($\mu\Omega$ cm)</th>
<th>$\rho$ (77 K) ($\mu\Omega$ cm)</th>
<th>$\alpha$ ($10^{-4}$ K$^{-1}$)</th>
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<tbody>
<tr>
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<td>14.0</td>
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<td>–</td>
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<tr>
<td>0</td>
<td>8.0</td>
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<td>250</td>
<td>–</td>
<td>–</td>
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<tr>
<td>61</td>
<td>0.3</td>
<td>–</td>
<td>220</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
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<td>1.7</td>
<td>–</td>
<td>230</td>
<td>–</td>
<td>–</td>
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<tr>
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<td>2.6</td>
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<tr>
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<td>340</td>
<td>364</td>
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<td>–</td>
</tr>
<tr>
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<td>–5.1</td>
<td>–</td>
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</table>
More detailed measurements [18] have shown that the temperature dependence of resistivity of the amorphous Al–W films, from LNT to RT, resembles that of amorphous TE–TL alloys, and can be well described in terms of weak localization of electrons [1].

The negative values of $\alpha$ in two Al–W films which contain traces of crystalline phase, indicate that the crystalline phase in these films is embedded into the amorphous matrix, so that the denoted range ($63 \leq x \leq 86$) represents a composition range for the reliable production of amorphous Al–W alloys. As for the amorphous-like tungsten, the two values for $R_H$, $\rho$, and $\alpha$, given in Table 1 indicate the limits of the observed values. These results are to be taken as preliminary. The influence of the sample preparation conditions onto the structure and electronic properties of amorphous-like tungsten ought to be further investigated in more detail.

### 4. Discussion

We note that for Al-rich amorphous alloys $R_H$ extrapolates to the values (which depend on the TM components) which are lower than that of pure liquid Al [8]. It can be argued that for still higher Al content, the electronic transport would be dominated by the sp-electrons. The addition of tungsten (or another TM element) to these hypothetical amorphous alloys would lead, in a simple picture of a charge transfer, to the decrease in number of free sp-electrons, and to the shift of $R_H$ to higher negative values. With further increase of TM concentration, the formation of the d-electron band sets in. This d-band would give rise to the sp–d hybridization, and to the effects of spin–orbit interaction which both lead to the deviation from the free-electron behaviour. Recent measurements of the electrical resistivity variations in the amorphous Al–W films above room temperature have shown that the relaxation effects in these films depends strongly on the alloy composition, and that the observed effects can also be related to the above mentioned formation of TM electron d-band [19].

For the TM amorphous alloys two important assumptions concerning the influence of the d-band upon the Hall effect are: (1) in the s–d hybridization [2], the d-band only modifies the s-electron band, while its direct contribution to the normal Hall effect is negligible [20]; (2) anomalous, i.e. spontaneous contribution is mainly due to spin–orbit interaction of the d-band conduction electrons [21]. Trudeau et al. [4,5] first argued that in TM amorphous alloys, the resistivity, paramagnetic susceptibility of d-band electrons, $\chi_d$, and their spin–orbit interaction, are all large enough to give a magnetic contribution to the measured $R_H$, which is comparable in magnitude to the expected free-electron value, $R_0$. In highly resistive alloys, this contribution, which we denote as $\Delta R_H = R_H - R_0$, is mainly due to the side-jump mechanism [22] and is proportional to the square of the resistivity, $\rho^2$. A brief discussion on the correlation between $R_H$ and $\rho$ in the amorphous alloys is given in Refs. [10,13,23].

As to the temperature dependence of $R_H$, there is relatively little data due to the small changes of $R_H$ with temperature [5,11,24–27]. The accurate measurements of the low temperature dependence of $R_H$ in some TE–TL alloys allowed the correlation with the quantum corrections in the electron–electron interaction [26,27]. However, these corrections are important only at low temperatures [1], far below the actual measuring temperatures, and we do not consider them here. Some data [5,11,24,25] for the temperature dependence of $R_H$ above LN temperature are taken [23] as evidence of the anomalous contribution to the $R_H$. It should be emphasized that if $\Delta R_H$ is due to the spontaneous contribution, then it should decrease as $\rho^2$, regardless of the actual sign of $R_H$.

In actual amorphous Al$_{x}$W$_{100-x}$ films the changes of the electrical resistivity from LNT to RT for $67 < x < 80$ are rather high [18] and of the order of 10%. Therefore, we have expected that, if there is a significant anomalous contribution to the Hall effect in these alloys, $R_H$ should have a significant temperature dependence. From the discussion at the beginning of this section we estimated that, for the selected alloys, the values for $R_H$ are more negative than that of liquid aluminum. From that observation, the values for $\Delta R_H = R_H - R_0$ are estimated to be of the order $10 \times 10^{-11}$ m$^3$ C$^{-1}$. Therefore, a decrease in the $R_H$ from LNT to RT of the order $1 \times 10^{-11}$ m$^3$ C$^{-1}$ has been expected. However, the values for $R_H$ determined for alloys
with 67 < x < 80 at liquid nitrogen and room temperature were the same within the experimental error which is equal to about 0.1 \times 10^{-11} \text{ m}^2 \text{ C}^{-1}. Therefore, these results do not support the proposition that there is a large spontaneous contribution to $R_H$ in these alloys which depend on the resistivity as $\chi d^2$.

In the above discussion we have neglected the possible effects of the temperature dependence of paramagnetic susceptibility. A temperature dependence of susceptibility in non-magnetic TE based amorphous alloys (especially in those doped with hydrogen) has been observed at low temperatures [28,29], below the actual measuring temperatures. The observed dependence of susceptibility on temperature has been interpreted in terms of electron–electron interaction, that we do not consider here. We also note that the quantities of the materials available to us (which are thin films and not rapidly quenched ribbons as in Refs. [10,28,29]) are not, at present, sufficient for the exact measurements of small magnetic susceptibility. Anyhow, there is no reason why would the ‘normal’ Pauli susceptibility increase with temperature so much as to overcome the decrease in the resistivity.

5. Conclusion

The room temperature values of Hall coefficient, $R_H$, electrical resistivity, $\rho$, and temperature coefficient of resistivity, $\alpha$, for thin $\text{Al}_x\text{W}_{100-x}$ films ($61 \leq x \leq 88$) have been reported. The films were prepared by magnetron co-deposition and were X-ray amorphous for $63 \leq x \leq 88$. Amorphous-like tungsten films ($x = 0$) were also obtained by sputtering at higher working gas pressure than that used for preparation of Al–W alloys. The $R_H$ value is strongly dependent upon the alloy composition. With the decrease of Al content, it changes sign from positive to negative value at $x \approx 78$, and exhibits a maximum for $x = 68$ at.%. At the same time, with the decrease of Al content, $\rho$ steeply increases and exhibits a maximum at $x = 80$ at.%. The temperature coefficient of resistivity exhibits large negative values, with a well defined minimum for $x = 80$.

The apparent correlation between $R_H$ and magnitude of $\rho$ can be attributed to the influence of the side-jump mechanism on the Hall effect. However, the values obtained for $R_H$ at LN temperature for films with $67 \leq x \leq 80$ were the same as the room temperature values. Since the value of electrical resistivity of these alloys in the temperature interval from 77 to 300 K varies noticeably (10%), a significant anomalous, i.e. spontaneous contribution to the Hall effect in amorphous Al–W alloys is not confirmed. This, together with the strong effects of temperature relaxation of Al–W films onto the electrical resistivity [19] supports the importance of the sp–d hybridization for the interpretation of the transport properties of amorphous Al–TM alloys.

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References