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Influence of argon pressure on the composition of Co–early transition metal films fabricated by r.f. magnetron sputtering in the composite target mode

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The effects of argon pressure and the solute element on compositional changes have been studied in binary Co–early transition metal (ETM) thin films fabricated by r.f. magnetron sputtering using the composite target mode. The solute concentration of the deposited film increases linearly with the area fraction of solute element of target and with the logarithm of argon pressure in the range 0.5–10 m torr. The compositional changes are discussed by considering not only the sputtering yield but also the argon pressure, which is related to the collision effect, and the difference in atomic weights between Co and ETM elements.

1. Introduction

Thin films of Co-based amorphous alloys containing early transition metal (ETMs) have been extensively studied because of their potential importance as head core materials for high-density recording [1, 2]. In order to make a good Co–ETM soft magnetic thin film, it is very important to control the composition, structure and impurity level of the film. Of several sputtering processes, the r.f. magnetron sputtering method is relevant to make a good Co–ETM thin film and has some merits in deposition rate and thickness control.

Though an alloy target is usually used in the sputtering process for mass production, it is very convenient to use a composite target in the laboratory because the solute concentration can be changed easily by controlling the area fraction of solute element chips put on the target. In the composite target mode, it is well known that the solute concentration of deposited film increases linearly with the area fraction of solute element chips, and the solute concentration difference between the target and the deposited film is interpreted in terms of the difference of sputtering yield between the constituent elements [3, 4].

In a sputtering process the film composition depends not only on the target composition but also on sputtering parameters such as the ionized gas pressure. However, the relation between the solute concentration and argon pressure has not been clearly established because of the complex collision effects of sputtered particles travelling from the target to the substrate.

In this work the effect of argon pressure on the change in the composition of binary Co–ETM thin films fabricated by r.f. magnetron sputtering in the composite target mode are investigated, and the results are compared with the theoretical equation. The correlation between the ratio of the solute concentration in the sputtered film to the area fraction of solute in the target and the sputter yield, the atomic weight and the argon pressure are also discussed.

2. Experimental procedure

Thin films were fabricated by an r.f. magnetron sputtering apparatus using the composite target mode. The target consisted of a pure cobalt disc with diameter 100 mm and small pieces of an ETM. A slide-glass with a thickness of 1 mm was used as a substrate and the substrate was water-cooled indirectly. The argon pressure during the sputtering was in the range 0.5 to 10 m torr, and the input power density was 1.23 to 1.64 W cm^{-2}. The composition of the sputtered film was analysed using an energy-dispersive X-ray spectrometer (EDS). The details of sputtering conditions used in the present work are summarized in Table I.

3. Results

Results for the solute concentration in the thin film (C_M) are shown in Fig. 1 as a function of the area fraction (A_M), which is defined as the ratio of area covered by solute element to that covered by Co target. The results are given for Co–Mo, Co–Nb,

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TABLE I Sputtering conditions for the composite target method

Parameter	Condition
Vacuum	8×10^{-7} torr
Ar pressure	0.5–10 m torr
Target (T)	Co disc (100 mm dia.), ETM plates (4 mm × 4 mm)
Substrate (S)	Slide glass (8 mm × 8 mm)
Distance T–S	7 cm
Power density	1.23–1.64 W/cm^{-2}
Thickness	1 μm

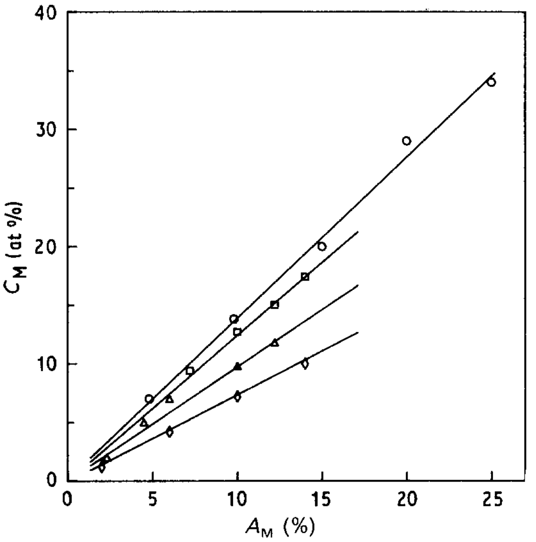

Figure 1 Solute concentration of thin films (C_M) as a function of the area fraction of solute elements on the target (A_M) for the binary thin films (○) Co–Mo, (□) Co–Nb, (△) Co–Zr and (◇) Co–V. Power density = 1.64 W cm^{-2}, P_{Ar} = 10 m torr.

Co–Zr and Co–V systems. The films shown in Fig. 1 were deposited at an argon pressure of 10 m torr and an input power density of 1.64 W cm^{-2}. It is seen from Fig. 1 that C_M increases linearly with A_M. This indicates that the ratio of the relative deposition rate of the transition metals to cobalt is constant. For a fixed value of A_M, the value of C_M is the highest for the Co–Mo system and decreases in the order of Nb, Zr and V.

In order to see how the argon pressure affects the relation between C_M and A_M, plots of C_M versus A_M at different argon pressure are shown in Fig. 2. The results shown are for the Co–Hf system and obtained at an input power density of 1.23 W cm^{-2}. The relation between C_M and A_M is also linear, similar to that shown in Fig. 1, for all the argon pressures used in the present work.

Fig. 3 shows the changes in C_M for the Co–Hf and Co–Y systems as a function of argon pressure, with sputtering at an input power density of 1.23 W cm^{-2}. It appears from Fig. 3 that the solute concentration increases linearly with the logarithm of argon pressure for both Co–Hf and Co–Y systems.

In this experiment the other sputtering parameters such as the input power density and the distance between target and substrate did not change the film composition within the analysis error range.

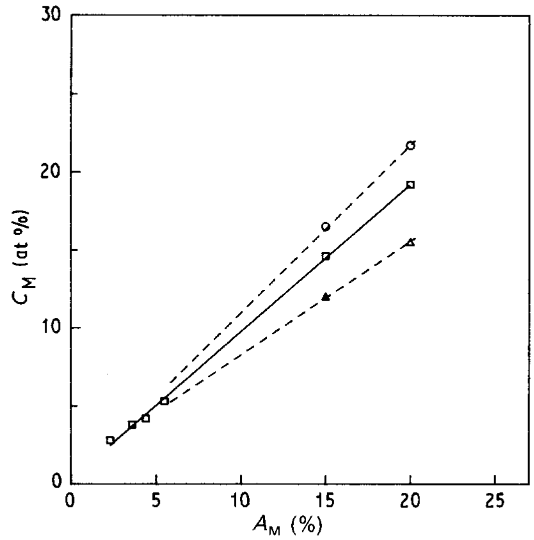

Figure 2 Relation between C_M and A_M for binary Co–Hf thin films. Power density = 1.23 W cm^{-2}; P_{Ar} = (△) 0.5 m torr, (□) 2 m torr, (○) 10 m torr.

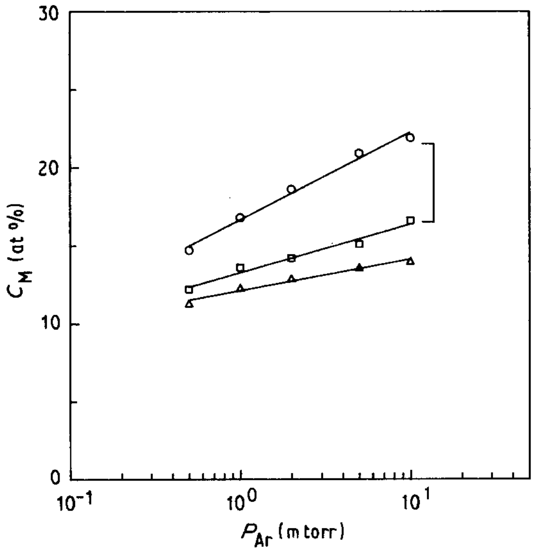

Figure 3 Change in solute concentration C_M as a function of argon pressure for binary (○, □) Co–Hf and (△) Co–Y thin films. Power density = 1.23 W cm^{-2}; A_M = (△) 0.12, (□) 0.15, (○) 0.20.

4. Discussion

The relation between C_M and A_M for films obtained by sputtering in the composite target mode has been suggested by other work [4, 5]. In an n-component system, the ratio is

$$\frac{C_i}{A_i} = \frac{kS_i}{\sum_{j=1}^{n} kS_j A_j} \qquad (1)$$

where the subscripts i and j refer to the elements used, k is a constant which is dependent on the sputtering apparatus and S is the sputter yield. For the same sputtering apparatus, Equation 1 can be written as

$$\frac{C_i}{A_i} = \frac{S_i}{\sum_{j=1}^{n} S_j A_j} \qquad (2)$$

In deriving Equations 1 and 2 it is assumed that the argon pressure does not affect the value of C_M/A_M. Since at a fixed argon pressure it is seen from Figs 1 and 2 that C_M/A_M is almost constant and is independent of A_i, we may obtain

$$\frac{C_i}{A_i} = \frac{S_i}{(1/n)\sum_{j=1}^{n} S_j} \qquad (3)$$

For the binary Co–M system Equation 3 reduces to $C_M/A_M = 2S_M/(S_M + S_{Co})$. In Fig. 4 are shown the results for C_M/A_M as a function of $2S_M/(S_M + S_{Co})$. The results shown in Fig. 4 were obtained from those shown in Figs 1, 2 and 3 at a constant argon pressure of 10 m torr. The value of S was taken from Laegreid and Wehner [5]. The theoretical results obtained from Equation 3 are indicated by the broken lines. For comparison the result obtained by Ouchi [6] for the Co–Cr system is also shown in Fig. 4. As can be seen from Fig. 4, the results for Co–V and Co–Cr systems are in good agreement with those predicted by Equation 3, whilst results for the other systems are in poor agreement, the values of C_M/A_M being larger than those predicted theoretically. The results, however, are within the region enclosed by the slopes 1 and 2 except for the result for Co–Cr.

The atomic weights and sputter yields for early transition metals are summarized in Table II. It is known from Table II and Fig. 4 that the values of C_M/A_M for elements with heavier atomic weights are larger than for those with lighter atomic weights. This may be due to differences in the scattering effect in the discharge space during sputtering: namely, the larger the atomic weight of the element is, the less the scattering of the element is. To investigate the effect of collision with Ar gas on C_M/A_M, the values of C_M/A_M are shown in Fig. 5 as a function of the atomic weight ratio of transition metal relative to argon element (M_M/M_{Ar}).

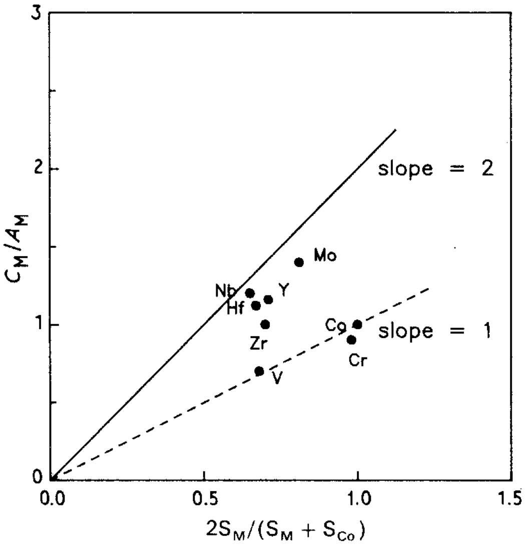

Figure 4 Change in C_M/A_M as a function of $2S_M/(S_M + S_{Co})$ for binary Co–M thin films. Power density = 1.23–1.64 W cm^{-2}; P_{Ar} = 10 m torr.

TABLE II Atomic weight and sputtering yield for the early transition metals studied

Element	Periodic table		Atomic weight M(g)	Sputtering yield, S (Ar$^+$, 600 eV)
	Column	Period		
Y	III$_B$	5	88.91	0.75
Zr	IV$_B$	5	91.22	0.75
Hf	IV$_B$	6	178.5	0.83
V	V$_B$	4	50.94	0.70
Nb	V$_B$	5	92.91	0.65
Cr	VI$_B$	4	52.0	1.30
Mo	VI$_B$	5	95.94	0.93
Co	VIII$_B$	4	58.93	1.36
Ar	VIII$_A$	3	39.95	–

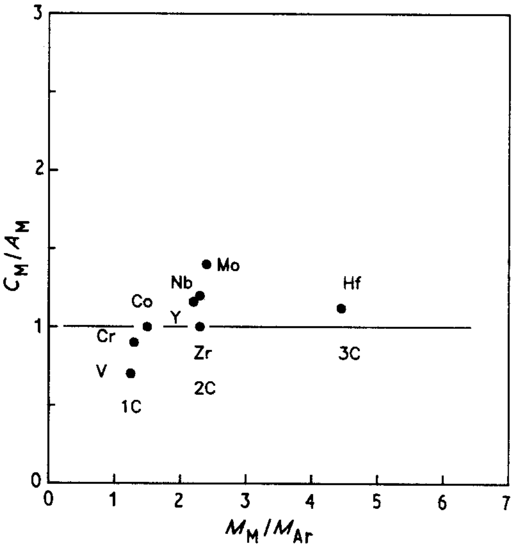

Figure 5 Change in C_M/A_M as a function of atomic weight ratio of transition metal relative to argon element (M_M/M_{Ar}) for binary Co–M thin films. Power density = 1.23–1.64 W cm^{-2}; P_{Ar} = 10 m torr.

This figure presents the following tendencies. Firstly, it is divided into three regions: V, Cr and Co elements lie in the first region, Zr, Y, Nb and Mo in the second region, and Hf in the third region. The elements which lie in each region belong to the same period in the periodic table of the elements. Secondly, C_M/A_M value of the transition metals which lie in each region increase broadly with the column in the table. This means that C_M/A_M tends to increase as the occupied d orbital increases. This trend is also related to that of the sputter yield S. Thirdly, C_M/A_M values for the elements in which C_M/A_M is a minimum in each period increase with the period.

Fig. 6 shows the change in $(C_M/A_M)/(M_M/M_{Ar})$ as a function of $2S_M/(S_M + S_{Co})$. In this figure, the trend is more linear than that of Fig. 4 except for the Co–Hf system in which the atomic weight of the solute is the highest among the present Co–ETM systems. The normalized results of Fig. 6 suggest that the atomic weight is an important parameter to explain the results for C_M/A_M. However, the slope value of 0.7 is physically meaningless. Also, the effect of the argon pressure on C_M/A_M cannot be explained by this relation. Our experimental results can be explained by taking the sputter yield and the argon pressure into

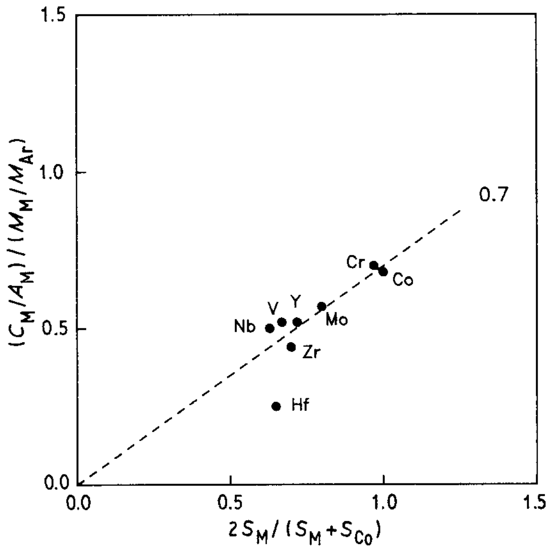

Figure 6 Change in $(C_M/A_M)/(M_M/M_{Ar})$ as a function of $2S_M/(S_M + S_{Co})$ for binary Co–M thin films. $P_{Ar} = 10$ m torr.

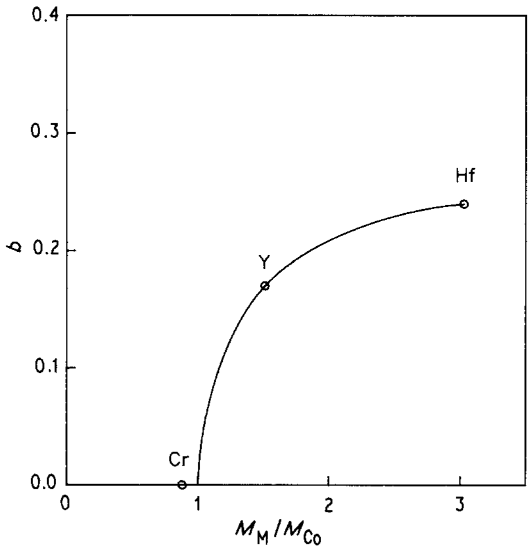

Figure 7 Relation between b values in Equation 6 and M_M/M_{Co}.

consideration simultaneously. Equation 3 can be expressed as follows by taking the argon pressure into consideration:

$$\frac{C_i}{A_i} = \frac{S_i}{(1/n)\sum_{j=1}^{n} S_j} f(P_{Ar}) \qquad (4)$$

As shown in Fig. 3, the concentrations of Hf and Y elements in films increase linearly with the logarithm of the argon pressure. Therefore the relation between C_M/A_M and the argon pressure can be given by

$$\frac{C_i}{A_i} = a + b \log(P_{Ar}) \qquad (5)$$

where a is a constant which depends on the sputter yield, b is a constant due to atomic weight differences of constituent elements, and P_{Ar} is the argon pressure. If the critical argon pressure at which C_M/A_M corresponds to $2S_M/(S_M + S_{Co})$ is P^c_{Ar}, Equation 5 can be expressed as

$$\frac{C_i}{A_i} = \frac{2S_M}{S_{Co} + S_M} + b \log\left(\frac{P_{Ar}}{P^c_{Ar}}\right) \qquad (6)$$

For Co–Hf and Co–Y systems P^c_{Ar} is 0.1 m torr. In Equation 6, as b is the constant due to atomic weight differences resulting in a scattering effect, b can be expressed by

$$b = c\left(\frac{M_M - M_{Co}}{M_{Co}}\right)^n \qquad (7)$$

By calculating Equation 6 from the results of Fig. 4, b is given to be about 0.24 and 0.17 for Co–Hf and Co–Y systems, respectively. Fig. 7 shows the relation between these values and M_M/M_{Co} of Equation 7. By fitting Equation 7 to Fig. 7, c and n are given to be 0.2 and 0.25, respectively. If these values are inserted in Equations 6 and 7, C_M/A_M can be expressed as follows:

$$\frac{C_i}{A_i} = \frac{2S_M}{S_{Co} + S_M} + 0.2\left(\frac{M_M - M_{Co}}{M_{Co}}\right)^{0.25} \log\left(\frac{P_{Ar}}{P^c_{Ar}}\right) \qquad (8)$$

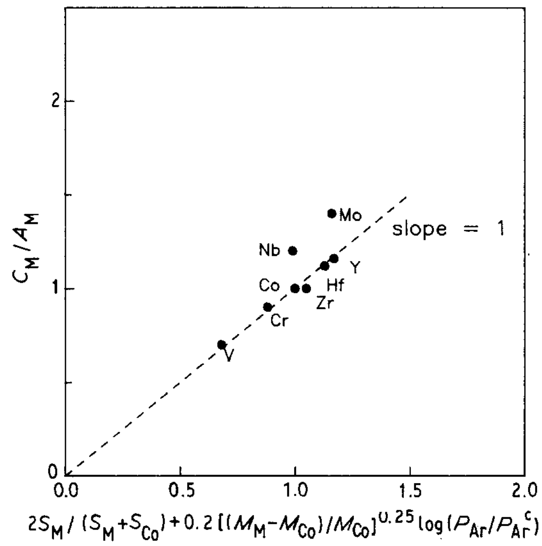

Figure 8 Change in C_M/A_M as a function of the value given by the right-hand side of Equation 8. Power density = 1.23–1.64 W cm^{-2}; $P_{Ar} = 10$ m torr.

In Equation 8, if the solute element has the same atomic weight as the solvent element, or the argon pressure is at the critical value P^c_{Ar}, C_M/A_M can be calculated simply from the sputter yields of the constituent elements. Otherwise, the atomic weight and the argon pressure must be taken into consideration to calculate C_M/A_M. Fig. 8 shows the changes in C_M/A_M at 10 m torr as a function of the value given by the right-hand side of Equation 8. In this figure, the trend appears that the gradient approaches much closer to unity than that in Fig. 4. Therefore it is confirmed that C_M/A_M values of early transition metals in binary Co–ETM thin films deposited in the composite target mode can be calculated by Equation 8.

5. Conclusion

The effect of argon pressure and the solute element on compositional changes in binary Co–ETM thin films fabricated by r.f. magnetron sputtering using the composite target mode is investigated. The concentration of solute atoms in the sputtered films increases linearly with the area fraction of solute element in the target, whilst the solute concentration increases linearly with the logarithm of the argon pressure in the range 0.5–10 m torr. It is believed that this is due to differences in the scattering effects of sputtered particles in the discharge space during the sputtering: the larger the atomic weight of the element is, the less the scattering of the element is. The correlation of the ratio of the solute concentration to the area fraction with the sputter yield, the atomic weight and the argon pressure is derived.

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