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Composition control of r.f.-sputtered $Ti_{50}Ni_{40}Cu_{10}$ thin films using optical emission spectroscopy

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Abstract

Optical emission spectroscopy can be used to monitor the composition of $Ti_{50}Ni_{40}Cu_{10}$ thin films during sputtering. The sputtering pressure can affect the spectrum intensity of Ni during r.f. magnetron sputtering, but has no obvious effect on that of Ti and Cu. This may be due to the ferromagnetic characteristic of Ni. By choosing peaks of Ti: 365.35 nm, Ni: 341.48 nm, Cu: 327.40 nm, we find that the peak intensity ratios of $I_{Ni,341.48}/I_{Ti,365.35}$ and $I_{Cu,327.40}/I_{Ti,365.35}$ remain constant in the range of 20–50 mTorr Ar pressure. The intensity ratio of these peaks is found to be proportional to the composition ratio of thin films with the relations: $Ni(\%)/Ti(\%) = 2.3817(I_{Ni}/I_{Ti}) - 0.8141$ and $Cu(\%)/Ti(\%) = 0.7427(I_{Cu}/I_{Ti}) + 0.1106$. Hence, the composition of sputtered thin films can be predicted by monitoring the intensity of light emission from the sputtering plasma. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: $Ti_{50}Ni_{40}Cu_{10}$ shape memory alloy; Sputtering; Optical spectroscopy; Ar pressure effect on peak intensity

1. Introduction

Thin films of Ti–Ni-based shape memory alloys (SMAs) play an important role in micro-electro-mechanical-system (MEMS) as SMAs have large deformation and strong recovery. However, the martensitic transformation temperatures of Ti–Ni SMAs are very sensitive to their composition. Though the addition of Cu in Ti–Ni thin films can reduce the sensitivity and hysteresis of transformation temperatures [1,2], accurate composition is demanded for industrial MEMS applications. Since the composition of sputtered thin film deviates from that of alloy target, the composition control of thin films of Ti–Ni SMAs is extremely important in the fabrication.

The composition of thin films is usually determined by the electron probe X-ray microanalysis (EPMA) after their deposition on the substrate. Besides using EPMA, monitoring the plasma concentration during sputtering is another feasible way. Optical spectroscopy has been widely used to monitor plasma etching, sputtering deposition and concentration analysis [3–5]. In this study, thin films of $Ti_{50}Ni_{40}Cu_{10}$ (at.%) SMA are sputtered on Si(100) wafers. In order to monitor the composition of sputtered $Ti_{50}Ni_{40}Cu_{10}$ thin films, optical emission spectroscopy is used to detect the plasma concentration during sputtering. The effect of Ar pressure during r.f. sputtering on the plasma intensity is also investigated. In addition, the relation between the peak intensity of plasma and the composition of sputtered thin films is discussed.

2. Experimental procedures

$Ti_{50}Ni_{40}Cu_{10}$ thin films are deposited on 3-in n-type Si(100) wafers by r.f. magnetron sputtering using a 2-in disk of $Ti_{50}Ni_{40}Cu_{10}$ target in argon atmosphere. The $Ti_{50}Ni_{40}Cu_{10}$ target has inserted disks of Ti and Cu to balance the greater loss of Ti and Cu atoms during sputtering. The sputtering conditions are as follows. The distance between the target and substrate is 6 cm. The base pressure is 2×10^{-6} Torr. The Ar pressure varies from 5 to 50 mTorr and the r.f. power is 200 W. Fig. 1 shows the sputtering system and optical spectrometer system used in this study. The light emission from the plasma is detected through a quartz window by a Jobin–Yvon Triax 320 monochromator and a R928 photomultiplier tube (PMT).

The spectral lines are obtained by scanning wavelength from 320 to 370 nm and are recorded in a computer. The scanning step is 0.07 nm. The peaks are chosen according to the study of Bendahan et al. [6,7] and the ‘MIT Wavelength Tables’ [8]. To prevent the loss of optical transmittance resulted from the deposition of Ti, Ni and Cu atoms on

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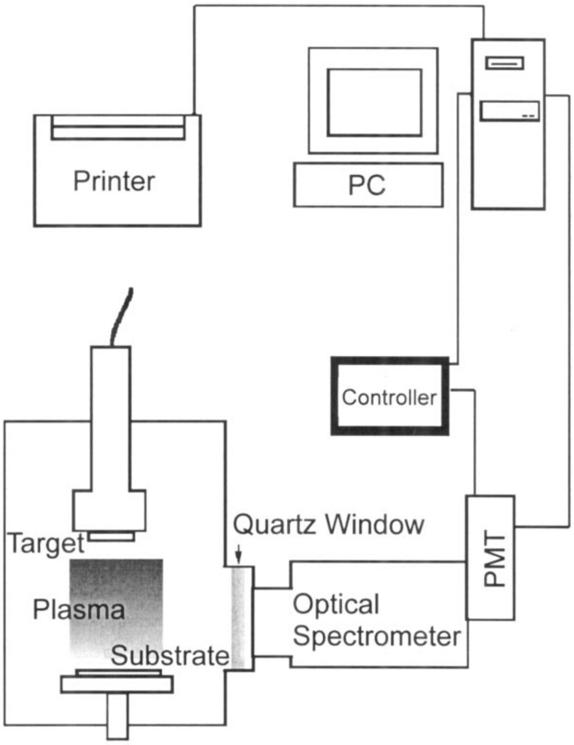

Fig. 1. Schematic representation of the experimental apparatus used in this study.

the quartz window, a clean quartz window is used after each scanning. In order to clean the contamination on the target surface and to get a stable glow discharge, the pre-sputtering time is chosen to be one hour before the deposition of thin films and the detection of plasma spectra. The compositions of sputtered $Ti_{50}Ni_{40}Cu_{10}$ thin films are determined by EPMA of a JEOL JXA-8600SX model.

3. Theoretical consideration

Optical spectroscopy is used to identify the relation between the intensity of light emitted from the plasma and the composition of thin films. The theoretical consideration is based on the assumption that the intensity of light emitted from the plasma is proportional to the concentration in the plasma [9–11]. The intensity of the spectral line corresponds to the transition of energy level in an atom. Most sputtered atoms ejected into the plasma region are neutral [12,13]. These atoms are directly impacted by electrons to an excited state

$$X + e \rightarrow X^{*} + e \qquad \text{rate } 1 = k_{\mathrm{e}}[X][e] \tag{1}$$

where X^* is referred to as the excitation state of X atom. In this study, X includes Ti, Ni, and Cu atoms. De-excitation process can occur in radiative decay and collisional quenching

$$X^{*} \rightarrow X + h\nu \qquad \text{rate } 2 = k_{\mathrm{r}}[X^{*}] \tag{2}$$

$$X^{*} + M \rightarrow X + M + (\text{kinetic energy of M})$$
$$\text{rate } 3 = k_{\mathrm{q}}[X^{*}][M] \tag{3}$$

where M represents Ar atom, h is the Planck's constant, ν is the frequency of light emitted, and k_{e}, k_{r} and k_{q} are the rate constants for the above three processes, respectively. At steady-state, the excitation rate is equal to the rate of radiative decay and collisional quenching, i.e. rate 1 = rate 2 + rate 3. From this relationship, $[X^*]$, the concentration of X^* in the plasma, can be represented as

$$[X^{*}] = \frac{k_e[X][e]}{k_{\mathrm{r}} + k_{\mathrm{q}}[M]} \tag{4}$$

The intensity of the spectral line is proportional to reaction (2) and can be written as

$$I \propto k_{\mathrm{r}}[X^{*}] = \frac{k_{\mathrm{e}}[X][e]}{1 + (k_{\mathrm{q}}/k_{\mathrm{r}})[M]} \tag{5}$$

Furthermore, the relative intensity ratio of Ni and Ti can be shown as

$$\frac{I_{\mathrm{Ni}}}{I_{\mathrm{Ti}}} = \left(\frac{[Ni]}{[Ti]}\right)\left(\frac{k_{\mathrm{e,Ni}}}{k_{\mathrm{e,Ti}}}\,\frac{1 + (k_{\mathrm{q,Ti}}/k_{\mathrm{r,Ti}})[Ar]}{1+(k_{\mathrm{q,Ni}}/k_{\mathrm{r,Ni}})[Ar]}\right) \tag{6}$$

Eq. (6) shows that the intensity ratio of spectral lines is proportional to the concentration ratio in the plasma. The

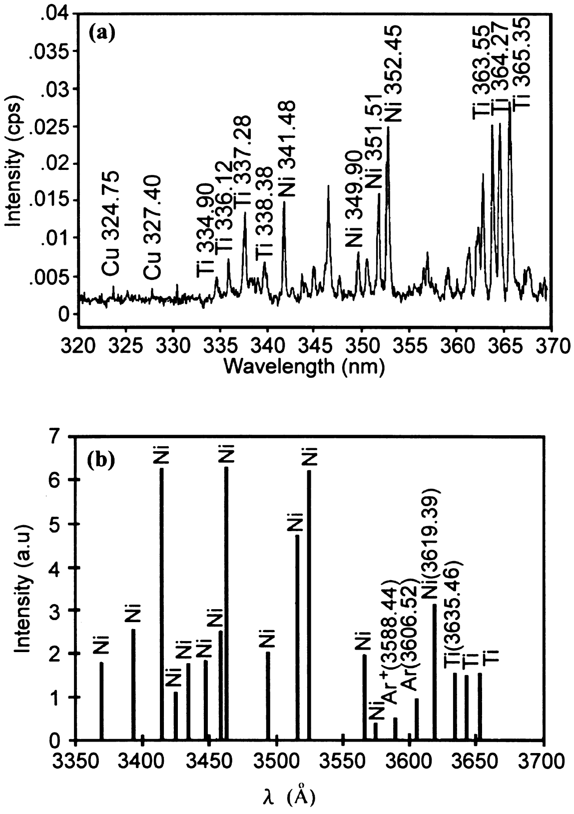

Fig. 2. (a) Spectrum of the plasma with $Ti_{50}Ni_{40}Cu_{10}$ alloy target in the wavelength from 320 to 370 nm. (b) Spectra of the plasma and the peaks chosen from Ref. [6].

larger round brackets on the right side of Eq. (6) is a constant under certain hypotheses. The excitation rate constant of Ni ($k_{e,Ni}$) depends on the threshold energy, the excitation cross section of Ni and the electron energy distribution function. The same situation can be given for $k_{e,Ti}$. So the larger round bracket can be considered to be a constant only if the Ni and Ti have approximately the same form of the excitation cross sections, the same threshold energies and that their excitation takes place from the ground state by direct electron impact. In the same way, I_{Cu}/I_{Ti} is proportional [Cu]/[Ti]

$$\frac{I_{Cu}}{I_{Ti}} = \left(\frac{[Cu]}{[Ti]}\right)\left(\frac{k_{e,Cu}}{k_{e,Ti}}\,\frac{1+(k_{q,Ti}/k_{r,Ti})[Ar]}{1+(k_{q,Cu}/k_{r,Cu})[Ar]}\right) \qquad (7)$$

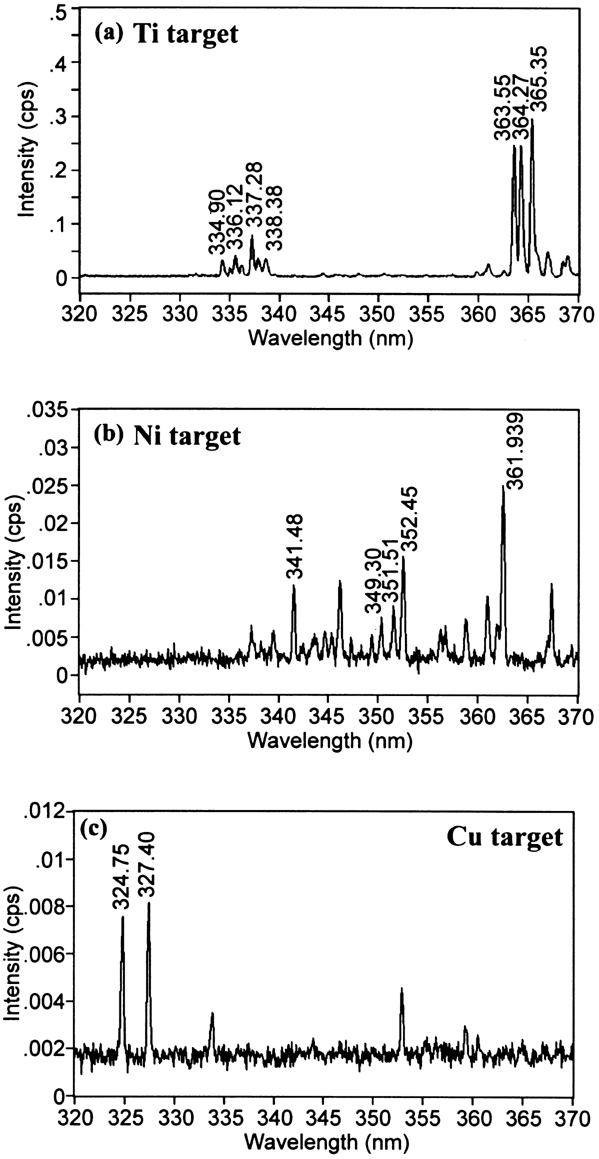

Fig. 3. Spectra of the plasma with targets of (a) pure Ti, (b) pure Ni, (c) pure Cu in the same wavelength range as in Fig. 2a.

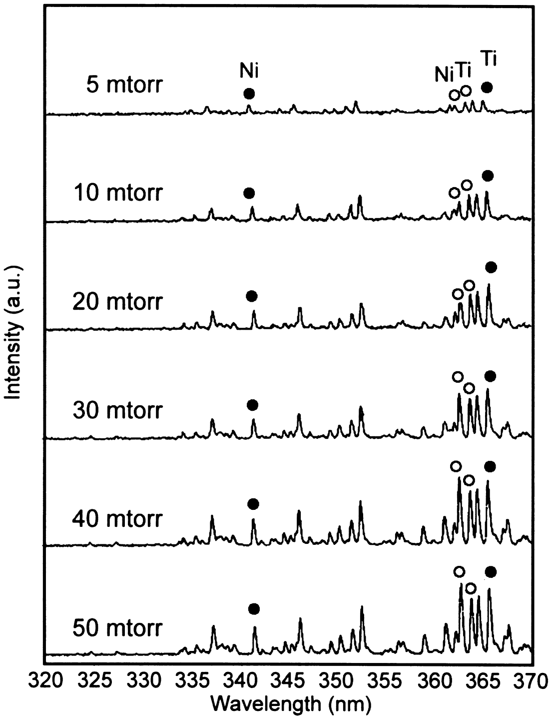

Fig. 4. Spectrum of the plasma with $Ti_{50}Ni_{40}Cu_{10}$ target under various Ar pressure. Hollow circles are 361.939 nm peak for Ni and 363.546 nm peak for Ti; solid circles are 341.48 nm peak for Ni and 365.35 nm peak for Ti.

4. Results and discussion

4.1. Plasma peaks detected by optical emission spectroscopy

Fig. 2a shows the spectrum from a glow discharge with $Ti_{50}Ni_{40}Cu_{10}$ target in the wavelength from 320 to 370 nm. Most of the peaks are due to Ti and Ni, with reference to the 'MIT Wavelength Tables' [8]. Compared with the peaks in the study of Bendahan et al. [6,7], as shown in Fig. 2b, a peak labeled as 361.939 nm is not listed in the 'MIT Wavelength Tables'. Therefore, it is necessary to identify this peak first. Fig. 3a,c show the spectra of the plasma with targets of pure Ti, pure Ni, and pure Cu, respectively. In Fig. 3, all peaks listed in the 'MIT Wavelength Tables' [8] are detected in the same range. The peak of 361.939 nm is due to Ni atoms, as shown in Fig. 3b. In Fig. 3, the unlabeled peaks may be due to Ar atoms [14].

Effect of Ar pressure on the spectrum of glow discharge with $Ti_{50}Ni_{40}Cu_{10}$ target is shown in Fig. 4. With reference to Fig. 4, the effect of the Ar pressure on the intensity ratios of $I_{Ni,361.939}/I_{Ti,363.546}$ and $I_{Ni,341.48}/I_{Ti,365.35}$ is plotted in Fig. 5. Bendahan et al. [6–7] chose two close and intense peaks, 363.546 nm peak for Ti and 361.939 nm peak for Ni, to study the relation between the plasma intensity and the thin film composition. These two peaks are labeled by hollow circles in Fig. 4. As seen in Fig. 5, the intensity ratio $I_{Ni,361.939}/I_{Ti,363.546}$ remains constant if the Ar pressure is lower than 20 mTorr, and this ratio increases quickly when the Ar pressure is higher than 20 mTorr. According to the 'MIT Wavelength Tables' [8], the 365.35 nm peak for Ti, 341.48 nm peak for Ni and 324.75 nm peak for Cu are much more sensitive than the others, although they are not the most intense ones. As seen in Fig. 5, the intensity ratio of $I_{\mathrm{Ni},341.48}/I_{\mathrm{Ti},365.35}$ (labeled by solid circles in Fig. 4) decreases gradually if the Ar pressure increases and is lower than 20 mTorr and then remains almost constant for Ar pressure $\geq$ 20 mTorr. This means that the tendency of the intensity ratios for $I_{\mathrm{Ni},361.939}/I_{\mathrm{Ti},363.546}$ and $I_{\mathrm{Ni},341.48}/I_{\mathrm{Ti},365.35}$ is quite different. In the next section, we will investigate the reason which causes this difference. Moreover, the plasma intensity of Ni being too weak to be detected by optical spectrometer if the Ar pressure is lower than 20 mTorr (Fig. 6) will also be discussed. Therefore, from Fig. 5, it seems more appropriate to choose $I_{\mathrm{Ni},341.48}/I_{\mathrm{Ti},365.35}$ to monitor the plasma intensity and to relate this intensity to the composition of sputtered $Ti_{50}Ni_{40}Cu_{10}$ thin films.

4.2. *Effect of Ar pressure on plasma intensity*

Fig. 6a,c are the plasma spectra under various sputtering pressure with targets of pure Ti, pure Ni and pure Cu, respectively. The relative spectrum intensity of Fig. 6 is listed in Tables 1–3. In Table 1, the intensity ratio of $I_{\mathrm{Ti},363.55}$, $I_{\mathrm{Ti},364.27}$ and $I_{\mathrm{Ti},365.35}$ is about 1:1:1.2 and is almost independent of the sputtering pressure. But in Table 2, the intensity ratio of $I_{\mathrm{Ni},341.48}$, $I_{\mathrm{Ni},349.30}$, $I_{\mathrm{Ni},352.45}$ and $I_{\mathrm{Ni},361.94}$ varies greatly with sputtering pressure, especially for the peaks of longer wavelength. Fig. 6b also shows that the light emission from plasma of pure Ni target is too weak to be detected under low Ar sputtering pressure, for example, below 20 mTorr. In Fig. 6c, the intensity ratio of $I_{\mathrm{Cu},324.75}$ and $I_{\mathrm{Cu},327.40}$ does not vary obviously with sputtering pressure.

The results of Fig. 6 show that only the relative spectrum intensity of Ni varies with sputtering pressure. Either the higher the Ar pressure or the longer the wavelength of Ni peak, the higher the peak intensity it has. Because Ni is a ferromagnetic metal, the Ni atoms ejected from the target can be influenced by the magnetic field during r.f. magnetron sputtering. From the Planck's theory of quantization

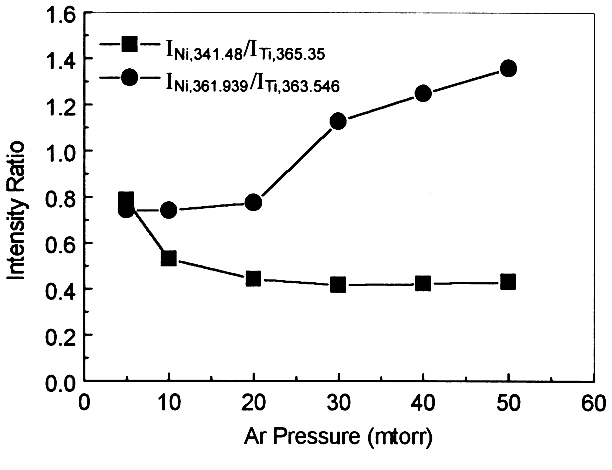

Fig. 5. The intensity ratios $I_{\mathrm{Ni},361.939}/I_{\mathrm{Ti},363.546}$ and $I_{\mathrm{Ni},341.48}/I_{\mathrm{Ti},365.35}$ versus Ar pressure.

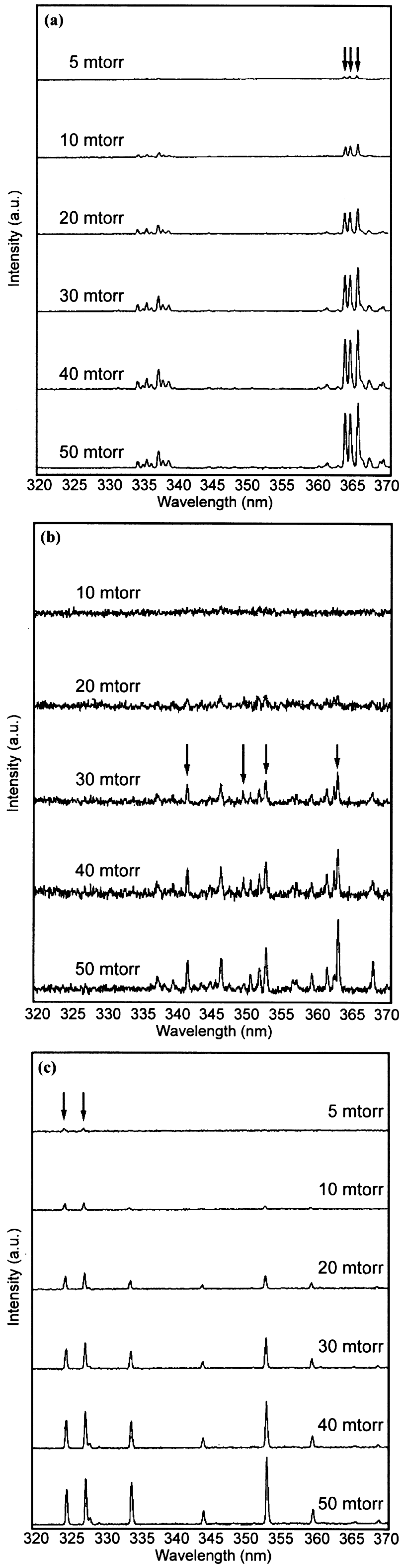

Fig. 6. Spectra of the plasma with targets of (a) pure Ti, (b) pure Ni and (c) pure Cu under various Ar pressure.

Table 1
Relative intensity ratio of peaks from Fig. 6a (unit: counts per second)

Sputtering pressure (mTorr)	Light emission wavelength (nm)			Intensity ratio
	363.55	364.27	365.35	
5	0.008343	0.008301	0.099949	1:0.995:1.198
10	0.043914	0.047123	0.054632	1:1.073:1.244
20	0.092885	0.094731	0.111481	1:1.020:1.200
30	0.162686	0.162856	0.194873	1:1.001:1.198
40	0.225452	0.222641	0.266711	1:0.988:1.183
50	0.245566	0.242038	0.291831	1:0.986:1.188

Table 2
Relative intensity ratio of peaks from Fig. 6b (unit: counts per second)

Sputtering pressure (mTorr)	Light emission wavelength (nm)				Intensity ratio
	341.48	349.30	352.45	361.939	
20	–	–	–	–	–
30	0.005735	0.006015	0.007045	0.009845	1:1.06:1.22:1.72
40	0.007624	0.008152	0.010132	0.015482	1:1.07:1.39:2.13
50	0.009836	0.010390	0.014031	0.023384	1:1.06:1.43:2.38

energy, $\Delta E = h\nu$, the light with longer wavelength comes from the transitions of electrons with closer energy levels. We suggest that the probability of these kinds of transitions may increase under the effect of magnetron sputtering.

4.3. Relation between the intensity ratio of plasma and the composition of thin film

In this study, we choose the more sensitive peaks, $I_{\mathrm{Ti},365.35}$, $I_{\mathrm{Ni},341.48}$ and $I_{\mathrm{Cu},327.40}$, to establish the relation between the intensity of plasma and the composition of the thin films. Fig. 7a,b plot the dependence of intensity ratio $I_{\mathrm{Ni}}/I_{\mathrm{Ti}}$ versus the composition ratio $C_{\mathrm{Ni}}/C_{\mathrm{Ti}}$ of $\mathrm{Ti}_{50}\mathrm{Ni}_{40}\mathrm{Cu}_{10}$ thin films and that of $I_{\mathrm{Cu}}/I_{\mathrm{Ti}}$ versus $C_{\mathrm{Cu}}/C_{\mathrm{Ti}}$, respectively. The appropriate equations of Fig. 7a,b are

$$\mathrm{Ni(at.\%)/Ti(at.\%)} = 2.3817(I_{\mathrm{Ni}}/I_{\mathrm{Ti}}) - 0.8141 \tag{8}$$

$$\mathrm{Cu(at.\%)/Ti(at.\%)} = 0.7427(I_{\mathrm{Cu}}/I_{\mathrm{Ti}}) + 0.1106 \tag{9}$$

Table 3
Relative intensity ratio of peaks from Fig. 6c (unit: counts per second)

Sputtering pressure (mTorr)	Light emission wavelength (nm)		Intensity ratio
	324.75	327.40	
5	0.002318	0.002895	1:1.248
10	0.005281	0.006664	1:1.262
20	0.012374	0.015601	1:1.261
30	0.018575	0.024380	1:1.314
40	0.026224	0.03446	1:1.313
50	0.032123	0.041942	1:1.306

According to Eqs. (8) and (9), as long as the intensity of light emission from the sputtering plasma is monitored, the composition of thin films can be predicted. Although the concentration ratio of plasma is not necessarily equal to

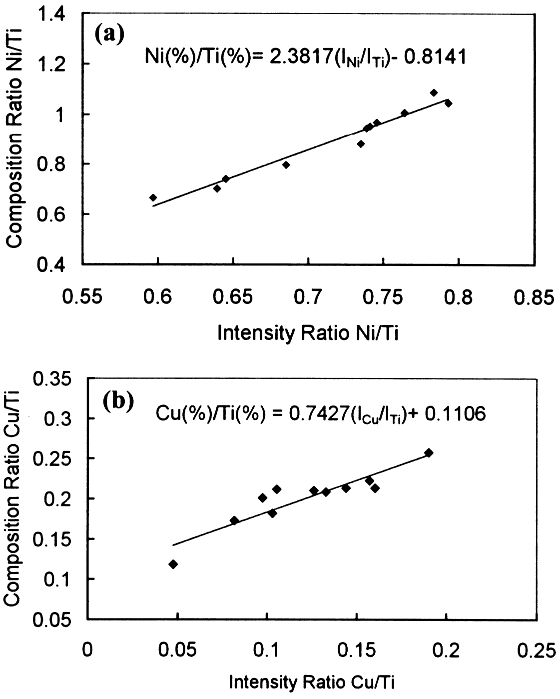

Fig. 7. (a) Intensity ratio $I_{\mathrm{Ni},341.48}/I_{\mathrm{Ti},365.35}$ versus composition $C_{\mathrm{Ni}}/C_{\mathrm{Ti}}$ of $\mathrm{Ti}_{50}\mathrm{Ni}_{40}\mathrm{Cu}_{10}$ thin films, (b) Intensity ratio $I_{\mathrm{Cu},327.40}/I_{\mathrm{Ti},365.35}$ versus $C_{\mathrm{Cu}}/C_{\mathrm{Ti}}$ of $\mathrm{Ti}_{50}\mathrm{Ni}_{40}\mathrm{Cu}_{10}$ thin films.

the composition ratio of thin films, we find that the optical signals are stable and reproducible. So the above equations can be used to monitor the composition of thin films.

5. Conclusions

Optical emission spectroscopy can be used to monitor the composition of $Ti_{50}Ni_{40}Cu_{10}$ thin films during sputtering. The sputtering pressure can affect the spectrum intensity of Ni during r.f. magnetron sputtering, but has no obvious effect on that of Ti and Cu. This may be due to the ferromagnetic characteristic of Ni. By choosing more sensitive peaks of Ti: 365.35 nm, Ni: 341.48 nm, Cu: 327.40 nm, we find that the peak intensity ratios of $I_{\mathrm{Ni},341.48}/I_{\mathrm{Ti},365.35}$ and $I_{\mathrm{Cu},327.40}/I_{\mathrm{Ti},365.35}$ remain constant in the range of 20–50 mTorr Ar pressure. The intensity ratio of these peaks is found to be proportional to the composition ratio of thin films. The relations are

$$\mathrm{Ni}(\%)/\mathrm{Ti}(\%) = 2.3817(I_{\mathrm{Ni}}/I_{\mathrm{Ti}}) - 0.8141$$

$$\mathrm{Cu}(\%)/\mathrm{Ti}(\%) = 0.7427(I_{\mathrm{Cu}}/I_{\mathrm{Ti}}) + 0.1106$$

Therefore, the composition of sputtered thin films can be predicted by monitoring the intensity of light emission from the sputtering plasma.

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