Irreversible hydrogen effects on resistivity of sputtered copper films

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Can hydrogen trapped within the lattice of copper film produce irreversible effects on the electrical resistivities of copper film at room temperature? In order to answer this question, copper films were sputtered in the presence of hydrogen and resistivities were measured in vacuum at room temperature. A series of sputtering depositions were carried out at different hydrogen partial pressures to confirm irreversible hydrogen effects. Films sputtered in argon only, were used as controls. The electrical resistivities of copper films were measured as a function of hydrogen partial pressure. Saturation is reached for the electrical resistivity in high hydrogen partial pressures. The saturation is at around 5.0% hydrogen partial pressure of total sputtering pressure. The electrical resistivities of copper films are lowered irreversibly by hydrogen, because the films were sputtered in the gas mixtures of argon and hydrogen and the electrical resistivities of films were measured in the air. The sputtering rate decreases as the hydrogen partial pressure increases. The sputtering rate is found to be proportional to the average mass of the incident ion.
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1. Introduction

Recently copper, as the interlevel metal in ULSI applications, has drawn considerable attention [1]. Compared to an aluminium thin film, copper offers low electrical resistivity, high heat capacity, high density, high thermal conductivity and high electromigration resistance. It is easily sputtered or electroplated. Also, with advent of chemical mechanical polishing (CMP) technology, the patterning of copper metal film, which was major problem of processing copper, was demonstrated successfully. In our study, hydrogen gas was introduced during sputtering copper film, in order to prove that it can lower resistivity of copper and characterize the effects of hydrogen on the electrical resistivity of copper. Gaseous hydrogen has been shown to affect the electrical properties of thin metallic films [2]. Recently, it was reported that the presence of hydrogen led to improvements in electrical properties of thin metallic films. Hydrogen has been shown to lower the electrical resistivity of thin metallic films, reduce the rate of electromigration in interconnect lines [3], and lower the stress generated in thin metallic films during annealing [4]. In this report, these effects will be referred to as hydrogen effects [5]. However, the biggest problem re-

lated to hydrogen effects is that hydrogen effects are reversible. In other words, hydrogen has effects on thin metallic films only in the closed chamber filled with hydrogen. A method to make hydrogen effects irreversible was studied. A possible mechanism by which hydrogen affects the electrical resistivities of thin metallic films at low temperature and room temperature are suggested.

2. Experimental procedure

The samples were prepared on three-inch p-type (100) silicon wafers. The oxidized wafers were attached to a steel sputtering plate by a binder clip and mounted inside the sputtering chamber. The mount for the sputtering plate was not fixed, so that the wafers could be rotated to improve uniformity during deposition. A copper sputtering target (99.9% Cu) was held in an US Inc. Magnetron sputtering gun 10 cm away from the substrate. The target was inclined 20 degrees to the plane of the substrate. Sputtering was only performed when the base pressure of the chamber was less than 10^{-6} Torr. Sputtering in argon and various gas mixtures of argon and hydrogen was performed at a pressure range of 6.2–7.1 mTorr, a current of 0.2 A, and a voltage range of

430–570 V. In all cases, after a 3-minute pre-sputtering was performed to clean the target right before sputtering, samples were sputtered for 7 minutes. After deposition, the samples were held in 10^{-7} Torr vacuum and allowed to cool back to the room temperature.

The sheet resistance of all samples were measured using a Veeco Instruments Inc. Model FPP −100 Four Point Probe System with the accuracy of ±0.5% of reading. Following sheet resistance measurement, steps to measure the copper film thickness were formed using standard photolithographic techniques. AZ-7510 photoresist was spun (700 rpm, 2 second spread, 5500 rpm, 30 second spin) onto the wafer. The sample was then baked in a MTI bake station for 60 seconds at 393 K. The sample was then placed in a GCA 6100 5× wafer stepper. The sample was exposed to ultraviolet light through a mask for 2 seconds. The sample was baked again in a MTI bake station for 60 seconds at 393 K.

The photoresist on the wafer was then developed for 60 seconds in AZ 300 MIF developer. After five-minute rinse in agitated deionized wafer, the sample was dried by blowing dry nitrogen over it. The sample was baked again in a MTI bake station for 60 seconds at 393 K. The etching solution was a mixture of 800 ml H_3PO_4, 50 ml HNO_3, 50 ml CH_3COOH, and 100 ml of H_2O [6]. The sample was etched in this solution for 60 seconds. The sample was then rinsed in agitated deionized wafer for 10 minutes. The sample was placed in PRS 3000 Photoresist Remover solution. The photoresist removal was done for 20 minutes at 341 K. The sample was then rinsed in agitated deionized wafer for 10 minutes. The sample was then placed in a Fluoroware Systems Dryer. The sample was spin-dried (450 rpm, 10 minutes). The thickness of copper films was measured using a Tencor Alpha-step 200 Profiler. The electrical resistivity of each sample was calculated from the sheet resistance and the thickness data.

3. Result and discussion

Cu film sputtering was done on the stripe of pre-made contacts, and the temperature measurement was done before, during, and after sputtering. I-V measurement was done right after sputtering. The data was converted to resistivity after thickness measurement. Fig. 1 shows the *in-situ*, time-dependent resistivity and temperature change of sputtered copper film in argon. The vacuum pressure right before the argon gas introduction was 4.9×10^{-7} Torr. Sputtering in argon only was performed at a pressure of 2.5 mTorr, a current of 0.4 A, and a voltage of 400 V. The temperature of the substrate was measured with RTD, which has a temperature resolution of 0.01 K. Sputtering began at the 7th minute and ended at the 11th minute. Right after the 4-minute sputtering, a Keithley Model 227 constant current source and a Keithley Model 195 A digital multimeter were turned on. The current setting was 1 mA with a total of accuracy of ±6.2 μA. The DC voltage range was 20 mV with a resolution of 100 nV. The voltage and temperature readings from digital multimeter were recorded to an IBM XT personal computer via IEEE-488 computer interfaces. Data were taken once a minute. Following the sputtering, the thickness of the copper film was mea-
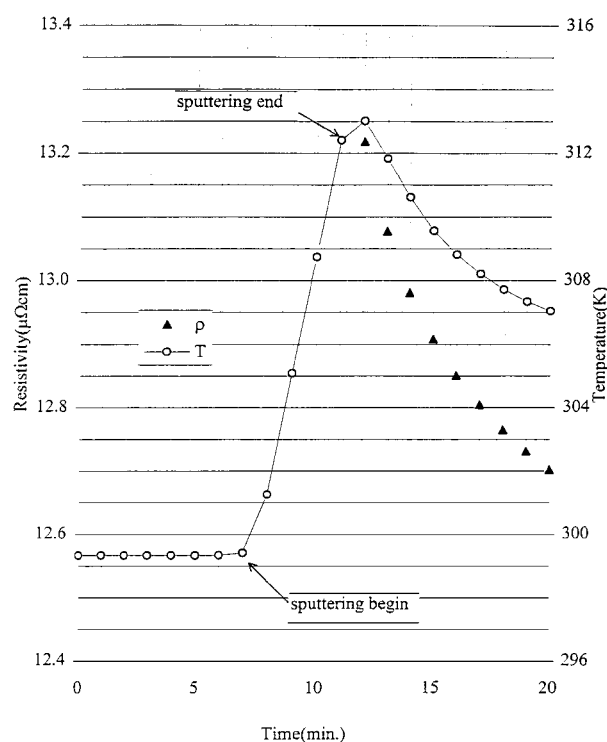

Figure 1 The *in-situ*, time-dependent resistivity and temperature changes of sputtered copper film in argon.
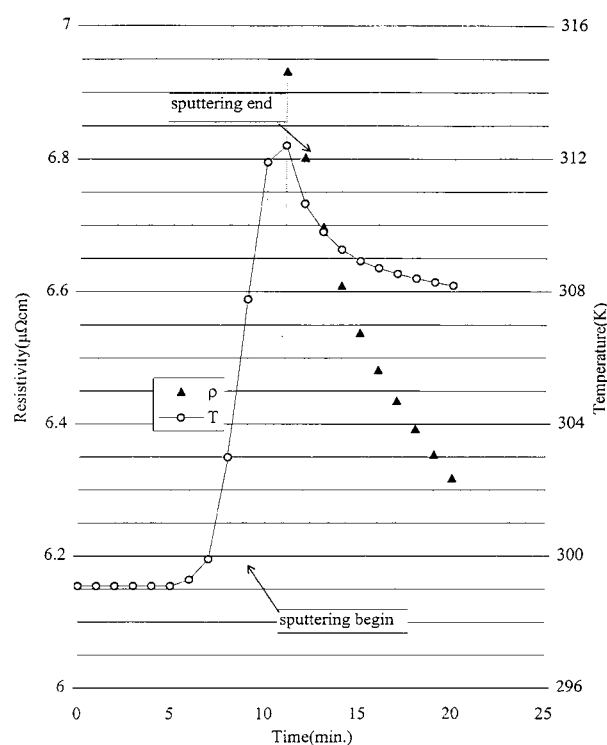

Figure 2 The *in-situ*, time-dependent resistivity and temperature change of sputtered copper film in an argon and 20% hydrogen gas mixture.

sured to be 1260 ± 25 Å by using a Tencor Alpha-step 200 Profiler. The width of the copper film sputtered in argon was 0.6 mm, and the length of the copper film was 9 mm. The electrical resistivity of the copper film was calculated from the resistance, the thickness, the width, and the length data of the copper film. Fig. 2 shows the *in-situ*, time-dependent resistivity and temperature change of sputtered copper film in an argon and 20% hydrogen gas mixture. The vacuum pressure right

before hydrogen gas introduction was 3.6×10^{-7} Torr. Hydrogen gas was introduced into the sputtering chamber first. The chamber pressure was 5.0×10^{-4} Torr after the hydrogen gas introduction. Then argon gas was introduced into the sputtering chamber. The total pressure of the sputtering chamber was 2.5 mTorr. Sputtering in thin 80% argon, 20% hydrogen gas mixture was performed at a current of 0.4 A and a voltage of 420 V. The experiment procedure was exactly same as that of argon gas only as described above. Sputtering began at the 7th minute and ended at the 10th minute. The final thickness of the copper film sputtered in an 80% argon and 20% hydrogen mixture was 713 ± 15 Å. The overall resistivity range of Fig. 2 (=6.1–6.9 $\mu\Omega$ cm) is considerably lower than that of Fig. 1 (=12.7–13.3 $\mu\Omega$ cm). The sputtering rate in 80% argon and 20% hydrogen gas mixture (=238 ± 5 A/min) was lower than that in argon only (=315 ± 6 Å/min). The sputtering rate is strongly affected by the presence of a hydrogen background in the sputtering chamber. Hydrogen has been found to reduce the sputtering rate in an argon discharge [7]. After the sputtering was done, the sputtering chamber pressure was 10^{-7} Torr range within less than 5 minutes. In Fig. 1, at 9 minutes after sputtering was done (the 20th minute), the chamber pressure was 6.3×10^{-7} Torr and the electrical resistivity of the copper film sputtered in argon only was 12.7 $\mu\Omega$ cm at 307 K. After 27 hours, the chamber pressure was 4.2×10^{-7} Torr and the electrical resistivity of the copper film sputtered in argon only was 11.4 $\mu\Omega$ cm at 298 K. In Fig. 2, at 9 minutes after sputtering was done (the 19th minute), the chamber pressure was 8.3×10^{-7} Torr and the electrical resistivity of the copper film sputtered in an 80% argon and 20% hydrogen gas mixture was 6.4 $\mu\Omega$ cm at 308 K. After 27 hours, the chamber pressure was 3.3×10^{-7} Torr and the electrical resistivity of the copper film sputtered in an 80% argon and 20% hydrogen gas mixture was 5.5 $\mu\Omega$ cm at 298 K. In both comparable cases, the electrical resistivities of the copper film sputtered in an 80% argon and 20% hydrogen gas mixture were considerably lower than those of the copper film sputtered in argon only. From these results, one can notice that the electrical resistivity of the sputtered copper film is lowered irreversibly by hydrogen. In this case, the effects of hydrogen are irreversible because the interactions between hydrogen and lattice defects are not limited to the surface and near surface region. If one simply replaces argon gas with an argon-hydrogen gas mixture, one can obtain the copper film of low resistivity after hydrogen gas has been removed. To confirm these results, a series of sputtering depositions were carried out at different partial pressure (PH$_2$). Table I shows the sputtering conditions and collected data of copper films sputtered in argon and various gas mixtures of argon and hydrogen. All sputtering conditions except the hydrogen partial pressures were constant. Sputtering conditions to produce poor films were used in order to clearly observe hydrogen effects. These sputtering conditions can be optimized to produce good films. The optimized background pressure and sputtering pressure were 1.9×10^{-7} Torr and 2.4 mTorr, respectively. Optimized sputtering in argon was performed at a current of 0.4 A and a voltage of 560 V. The as-deposited resistivity of the sputtered copper film in argon was 2.3 ± 0.05 $\mu\Omega$ cm. Optimized sputtering in a 90% argon and 10% hydrogen gas mixture was performed at a current of 0.4 A and a voltage of 600 V. The as-deposited resistivity of the sputtered copper film in a 90% argon and 10% hydrogen gas mixture was 2.2 ± 0.05 $\mu\Omega$ cm. In these cases, a hydrogen effect is perhaps observed but it is within the range of twice the reproducibility (± 0.05 $\mu\Omega$ cm). The background pressure right before the gas introductions was 6.5–7.6×10^{-7} Torr. Sputtering in argon and various gas mixtures of argon and hydrogen was performed at a pressure (PS) range of 6.0–7.3 mTorr, a current (I) of 0.2 A, and a voltage range of 430–570 V. In all cases, a 3-minute pre-sputtering was performed to clean the target right before sputtering, and then samples were sputtered for 7 minutes (t). After deposition, the samples were held in 10^{-7} Torr order vacuum and allowed to cool back to the room temperature. Fig. 3 shows the effects of hydrogen partial pressures on the sputtering rate (r). The sputtering rate decreases as the hydrogen partial pressure increases. This confirms the *in-situ* measurement results above. The sputtering rate is determined by the sputtering yield [8]. The sputtering yield is defined as the number of atoms or molecules ejected from a target surface per incident ion, and is a measure of the efficiency of sputtering [9].

TABLE I The sputtering conditions and collected data of copper films sputtered in argon and various gas mixtures of argon and hydrogen

PH$_2$ (%)	PB (Torr)	PS (mTorr)	I (A)	t (min.)	R_S (mΩ/)	t_i (Å)	r (Å/mim)	m_i (g/mol)	ρ ($\mu\Omega$ cm)	$\langle n_{v,i} \rangle$ (10^{18}/Å)
0.0	7.6×10^{-7}	6.0–6.2	0.2	7.0	1850	2000	286	39.9	37.0	11.8
3.0	7.5×10^{-7}	6.6–6.8	0.2	7.0	671	1880	269	38.8	12.6	3.87
5.0	7.4×10^{-7}	6.2	0.2	7.0	193	1400	200	38.0	2.70	0.487
10	6.8×10^{-7}	6.6–6.9	0.2	7.0	226	1260	180	36.1	2.85	0.620
20	6.2×10^{-7}	6.8–7.3	0.2	7.0	301	925	132	32.2	2.78	0.794
30	7.2×10^{-7}	6.4–6.5	0.2	7.0	596	485	69.0	28.3	2.89	1.67

PB: Background pressure.
PS: Sputtering pressure.
R_S: Sheet resistance.
t_i: Film thickness.
r: Sputtering rate.
m_i: The average mass of the incident beam.
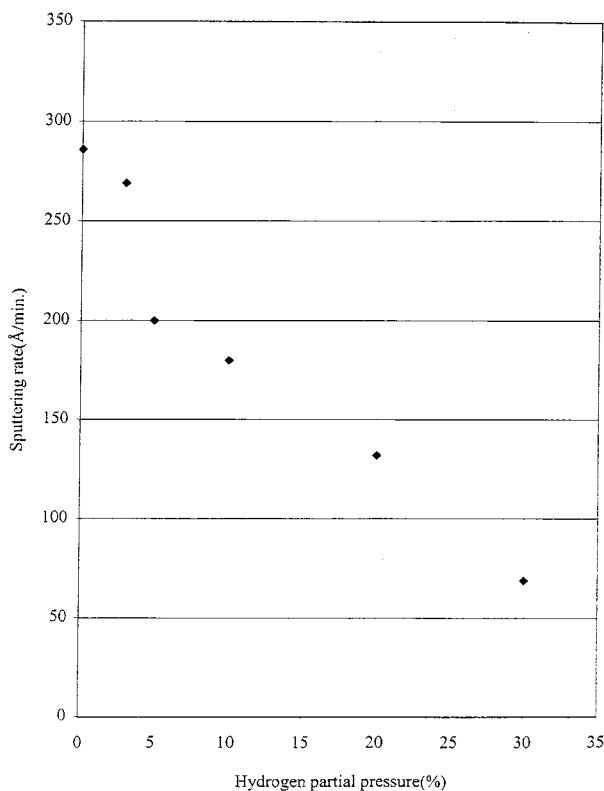$\langle n_{v,i} \rangle$: The number of vacancies per unit thickness.

Figure 3 The effects of hydrogen partial pressures on the sputtering rates (*r*).

Figure 4 The relationship between hydrogen partial pressures and the average masses of the incident ion.

In the energy range of practical interest for sputtering processes (10–5000 eV), the sputtering yield increases with mass of the incident ion [10–14]. The sputtering yield was shown by Moore [15] to be a strong function of ionic mass. He reported that the yield is 50 times greater for neon (5-keV ions incident on silver) than it is for deuterium, although the ratio of ionic masses is only 10. Hence one would not expect a significant sputtering contribution by the hydrogen ions. However, the hydrogen ions will clearly contribute to the observed sputtering current. In other words, the hydrogen ions will clearly contribute to the observed sputtering current but not to sputtering material flux [7]. As the hydrogen partial pressure was increased, more hydrogen ions contribute to the cathode current but not to the sputtered copper flux. Since the cathode current was constant (0.2 A) in this study, the sputtering rate should decrease as the hydrogen partial pressure increases. This can be explained in the following way. In this study, the chamber volume and total pressure are identical in all cases. From the partial pressures of argon and hydrogen gas mixture, molecular masses of hydrogen and argon, the average mass of the incident ion (m_i) was calculated. The calculated m_i values (g/mol) are shown in Table I.

Fig. 4 shows the relationship between hydrogen partial pressures and the average masses of the incident ion. The average mass of the incident ion decreases as the hydrogen partial pressure increases. The sputtering rate is found to be proportional to m_i. In other words, as more hydrogen molecules are involved in the sputtering process, the average mass of the incident ion decreases. Therefore as hydrogen partial pressure increases, the sputtering rate deceases. Fig. 5 shows the effects of hydrogen partial pressures on the electrical resistivity. The
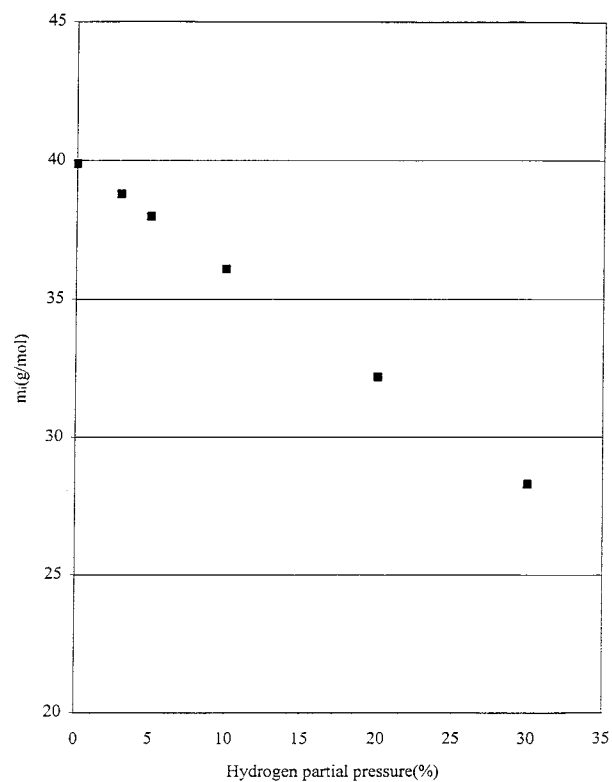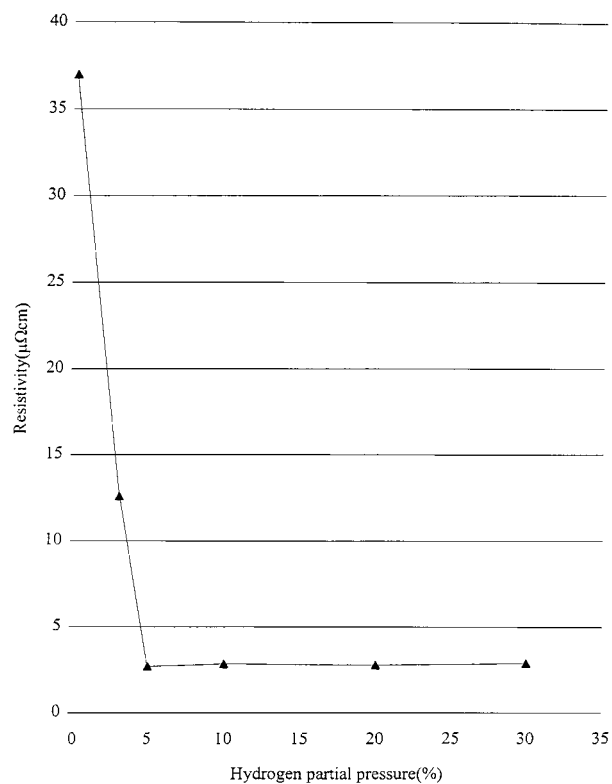

Figure 5 The effects of hydrogen partial pressures on the electrical resistivities.

electrical resistivity (ρ) of each sample was calculated from the measured sheet resistance (R_S) and the measured thickness (t_i) data. A lower limit is reached for the electrical resistivity in high hydrogen partial pressures. The limit occurs near $PH_2 = 5.0\%$. These results confirm that the electrical resistivity of the sputtered

copper film is lowered irreversibly by hydrogen because the measured resistivity is the as-deposited resistivity in the air. In order to explain these results, the interactions between hydrogen and defects are considered. Hydrogen stimulates the formation of vacancy clusters [16]. In other words, hydrogen can reduce the effective defects densities of thin metallic films. In general, for a close-packed crystal such as copper, the concentration of self-interstitials is insignificant compared with the concentration of vacancies in the crystal [17]. If the electrical resistivity increment of a vacancy is ρ_v and the number of vacancies is $n_{v,i}$, the electrical resistivity of the sample is given by

$$\rho_i = \rho_p + n_{v,i} + \rho_v \tag{1}$$

where ρ_p is the resistivity of a crystal containing no vacancies [17].

$$\rho_i - \rho_p = n_{v,i}\rho_v \tag{2}$$

Since the resistivity measurements were done at room temperature, ρ_p is a constant. ρ_p of copper at 293 K is $1.678\,\mu\Omega$ cm [18] and ρ_v is $1.5 \times 10^{-21}\,\mu\Omega$ cm per vacancy [19].

Therefore,

$$n_{v,i} = (\rho_i - 1.678\,\mu\Omega\,\text{cm})/$$
$$1.5 \times 10^{-21}\,\mu\Omega\,\text{cm per vacancy} \tag{3}$$

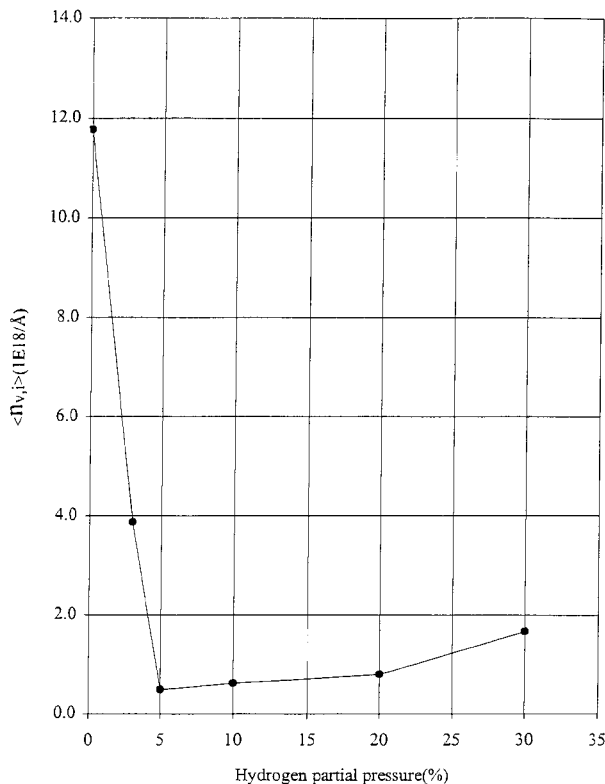Since the film thickness of samples are different, $n_{v,i}$ are normalized to film thickness. The number of vacancies

per unit thickness ($\langle n_{v,i} \rangle$ (#/Å)) of the sample is given by

$$\langle n_{v,i} \rangle = n_{v,i}/t_i \tag{4}$$

The calculated values of $\langle n_{v,i} \rangle$ are shown in Table I. Fig. 6 shows the effects of hydrogen partial pressures on the number of vacancies per unit thickness. There is saturation at around 5.0% hydrogen partial pressure of total sputtering pressure. Even though the hydrogen reduces the sputtering rates, the hydrogen introduction during sputtering is useful. The electrical resistivities of as-deposited films sputtered in argon and hydrogen gas mixtures are as good as post-deposition annealed films sputtered in argon only. By simply replacing an argon gas cylinder with an argon and hydrogen gas mixture cylinder, one can eliminate the post-deposition annealing steps. The important point is that one can make irreversibly low resistivity thin metallic film without modifying any processing step or equipment.

4. Conclusion

Can hydrogen trapped within the lattice produce irreversible effects on the electrical resistivities of copper film at room temperature? In order to answer this question, copper films were sputtered in the presence of hydrogen and resistivities were measured in vacuum at room temperature. Films sputtered in argon only, were used as controls. A series of sputtering depositions were carried out at different hydrogen partial pressures to confirm irreversible hydrogen effects. Base upon those experiment and the subsequent analysis, the following conclusions were drawn. The electrical resistivities of copper films are lowered irreversibly by hydrogen, because the films were sputtered in various gas mixtures of argon and hydrogen and the electrical resistivities of films were measured in the air. The sputtering rate decrases as the hydrogen partial pressure increases. The sputtering rate is found to be proportional to the average mass of the incident ion.

References

1. T. OHMI, T. SATIO and T. SHIBATA, in Proc. 5th Int. IEEE VLSI Multilevel Interconnection Conf. IEEE Cat. #88CH 2624-5 (IEEE, NY, 1988) p. 135.
2. C. APBLETT, D. MUIRA, M. SULLIVAN and P. FICALORA, *J. Appl. Phys.* **10**(71) (1992) 4926.
3. K. RODBELL and P. FICALORA, *ibid.* **65**(8) (1989) 3107.
4. C. APBLETT and P. FICALORA, *ibid.* **69**(8) (1991) 4431.
5. C. APBLETT, Ph. D. thesis, Rensselaer Polytechnic Institute, Troy, NY, 1992.
6. D. ELLIOT, "Intergrated Circuit Fabrication Technology" (McGraw Hill, NY, 1982).
7. E. STERN and H. CASWELL, *J. Vac. Sci. & Tech.* **4**(3) (1967) 128.
8. J. VOSSEN and W. KERN, (eds.), "Thin Film Processes" 2nd ed. (Academic Press, NY, 1978).
9. A. GLASER and SUBUK-SHARPE, "Integrated Circuit Engineering" (Addison Wesley, Reading, MA, 1979).
10. G. WEHNER, Rep. No. 2309, General Mills, Minneapolis, 1962.
11. C. WEYSENFELD and A. HOOGENDOOM, in 5th Proc. Conf. Ion. Phenom. Gases, Munich 1, 1961, p. 24.
12. D. MCKEOWN and A. CABEZAS, Annu. Rep. Space Sci. Lab., General Dynamics, July 1962.

Figure 6 The effects of hydrogen partial pressures on the number of vacancies per unit thickness.

13. P. ROL, J. FLUIT and J. KISTEMAKER, "Electromagnetic Separation of Radioactive Isotopes" (Springer-Verlag, NY, 1960).

14. O. ALMEN and G. BRUCE, in 8th Trans. Natl. Vac. Symp., Washington D.C., 1961, p. 245.

15. W. MOORE, *Am. Scientist* **48** (1960) 116.

16. J. CONDON and T. SCHOBER, *J. Nuclear Materials* **207** (1993) 1.

17. R. SWALIN, "Thermodynamics of Solid" (John Wiley & Sons, NY, 1972).

18. R. WEAST, (Ed.), "CRC Handbook of Chemistry and Physics," 70th ed., F-146 (CRC Press, Inc., Boca Raton, FL, 1990).

19. G. MEADEN, "The Electrical Resistance of Metals" (Plenum Press, NY, 1965).