Optical emission spectroscopic study on H-assisted plasma for anisotropic deposition of Cu films

Jun Umetsu, Kazuhiko Inoue, Kazunori Koga and Masaharu Shiratani
Department of Electronics, Kyushu University, Fukuoka, Japan
j.umetsu@plasma.ed.kyushu-u.ac.jp

Abstract. We have studied dependence of $H\alpha$ intensity and electron density on the discharge power and gas flow rate ratio $R = H_2/(H_2 + Ar)$, to obtain information on a discharge condition bringing about a high H flux to film surfaces, because irradiation of H atoms on surfaces removes impurities in films and enhances the deposition rate. The highest $H\alpha$ intensity, which is obtained for the discharge power of 500 W and $R=\text{3.3\%}$, is 10 times as high as that for previous deposition condition of the discharge power of 150 W and $R=\text{11\%}$. Moreover, emission spectra suggest Ar metastable contribute to H generation for $R=\text{3.3-33\%}$.

1. Introduction
Filling of materials in trenches and holes of nm scale is important for fabrication of three dimensional nano-structures such as ULSI interconnects, quantum dots and wires, micro-electrochemical systems, and system in package. Although Cu interconnects in ULSI have been fabricated by seed-layer deposition using physical vapor deposition (PVD) and subsequent filling using electroplating, the former deposition becomes difficult owing to reduction in the feature size of trenches and via holes. PVD usually results in subconformal deposition profile in trenches. For a narrow trench of a high aspect ratio, such subconformal deposition results in a keyhole in the trench. Plasma and thermal chemical vapor depositions (CVDs) realize conformal filling in trenches. The conformal filling, however, results in a small crystal grain size below half of the trench width and also in a seam where impurities of high concentration remain. To solve these problems, we have realized anisotropic deposition of Cu films, for which Cu is filled preferentially from the bottom of trenches without being deposited on the sidewall of trenches [1, 2]. Figure 1 shows a typical cross section SEM image of Cu deposited in a trench by plasma anisotropic CVD. The anisotropic deposition is useful for fabricating nano-structures such as nano-scale interconnects, because it has two interesting features. One is the fact that the narrower the width of trench is, the faster the deposition rate on its bottom becomes. The other is the self-limiting deposition, that is, the deposition in the trench stops automatically just after filling it completely. Ion irradiation on the surfaces of interest is the key to realizing the anisotropic deposition, since the deposition rate on the bottom surface of trenches increases with the flux and kinetic energy of ions impinging on the surface. Moreover, irradiation of H atoms on the surfaces removes impurities in films and enhances the deposition rate.

In this paper, we report dependence of $H\alpha$ intensity and electron density on the discharge power and gas flow rate ratio of $H_2$ to Ar, to obtain information on a discharge condition bringing about a high H flux to film surfaces.
2. Experimental
Experiments were carried out using a reactor, in which a capacitively-coupled main discharge and an inductive-coupled discharge for an H atom source were sustained. This reactor provided independent control of densities of Cu-containing radicals and H atoms. For the main discharge, the mesh powered electrode of 85mm in diameter and the plane substrate electrode of 85mm in diameter were placed at a distance of 30 mm. The discharge frequency of the main discharge was 28MHz and the supplied power was below 50W. The discharge of H atom source was sustained with an rf induction coil of 100 mm in diameter placed at 65 mm above the substrate electrode of the main discharge. The discharge frequency of H atom source was 13.56 MHz and the supplied power was below 500W. Ar + H2(0-100%) gases were supplied at a total flow rate of 90 sccm. The total pressure was 13 Pa.

Optical emission intensities from the inductively coupled discharge were measured at 20 mm above the center of the substrate electrode with an optical multi-channel analyzer (Hamamata Photonics PMA-11-C7473). Electron density, ne, was measured with a plasma absorption probe. [3]

3. Results and Discussion
First, to obtain information on a discharge condition bringing about a high H flux to film surfaces, we have studied dependence of H\(\alpha\) emission intensities on the discharge power of H atom source as a parameter of the gas flow rate ratio \(R = H_2/(H_2 + Ar)\). Figure 2 shows the results. Both the intensity is weak for the CCP discharge mode in a low power range and it increases linearly with the power for the ICP mode. The highest H\(\alpha\) intensity, which is obtained for the discharge power of 500 W and \(R=3.3\%), is 10 times as high as that for previous deposition condition of the discharge power of 150 W and \(R=11\%\).

Next, we have measured electron density using the plasma absorption probe. Figure 3 shows dependence of electron density on the discharge power of H atom source. The electron density increases in a sub-linear way with the discharge power.

We briefly discuss elementary processes for the emission intensity. The electron impact excitation processes for H\(\alpha\) emission are as follows,

\[
\begin{align}
H_2 + e(slow) &\rightarrow H(n=3) + H + e(slow) \rightarrow 2H + e(slow) + h\nu \\
H + e(fast) &\rightarrow H(n=3) + e(slow) \rightarrow H + e(slow) + h\nu
\end{align}
\]

The excited state \(H(n=3)\) for H\(\alpha\) emission is formed through the electron impact dissociative excitation reaction of \(H_2\) and the excitation reaction of H. [4] Therefore, the intensity is expressed as follows,

\[
I_{H\alpha} = c_1\tau_1(\sigma_1\nu_e)n_e[H_2] + c_2\tau_2(\sigma_2\nu_e)n_e^2[H_2]
\]

where \(I, \tau, \sigma, \nu_e, n_e, c\) are the emission intensity, lifetime of the excited states, cross section for the excitation, thermal speed of electrons, electron density, and a proportion constant. [\] denotes the density of species in it.
Figure 2. Dependence of $H\alpha$ intensity on discharge power of H atom source as a parameter of gas flow rate ratio (R).

Figure 3. Dependence of electron density, $n_e$, on discharge power of H atom source as a parameter of gas flow rate ratio (R).

Figure 4. Dependence of $H\alpha$ intensity normalized by $H_2$ density on electron density, $n_e$ as a parameter of R.

Dependence of the emission intensity ratio of $H\alpha/H_\beta$ on electron density is evaluated as shown in Fig. 5, since the ratio contains information about the dissociation degree of $H_2$ [4]. The intensity ratio decreases with increasing the dissociation degree when the electron impact excitation processes such as (1) and (2) are predominant for $H\alpha$ and $H_\beta$ emissions [4]. The ratio, however, is nearly constant for $R=11\%$ and increases significantly with $n_e$ for $R=3.3\%$ and 6.7\%. These results suggest that another excitation processes, such as an excitation transfer from metastable Ar to $H_2$, contribute to the emissions, since the dissociation degree of $H_2$ increases with with $n_e$. 
Finally, to obtain information about effects of Ar metastable on H generation, we have studied emission spectrum in a wavelength range from 200 to 400 nm as shown in Fig. 6. The continuous emission spectrum intensity is identical for R=100-50%, increases significantly with decreasing R from 50 to 11%, then it saturates for R=11-3.3%. This emission is assigned to the UV chemiluminescence of the ArH(B2Π—X2Σ+) transition due to the reactions of Ar(4s3P2) and Ar(4s'3P0) metastable atoms with H2 [5]. The reactions generate H atoms. Therefore, these results indicate that such H generation processes become important for R=33-3.3%.

4. Conclusions
We have studied dependence of Hα intensity and electron density on the discharge power and gas flow rate ratio R = H2/(H2 + Ar), to obtain information on a discharge condition bringing about a high H flux to film surfaces, because irradiation of H atoms on surfaces removes impurities in films and enhances the deposition rate. The highest Hα intensity, which is obtained for the discharge power of 500 W and R=3.3%, is 10 times as high as that for previous deposition condition of the discharge power of 150 W and R=11%. Moreover emission spectra suggest Ar metastable contribute to H generation for R=3.3-33%.

Acknowledgement
This work was partly supported by a grant from the Japan Society of the Promotion of Science.

References
[1] K. Takenaka, M. Shiratani, M. Onihsi, M. Takeshita, T. Kinoshita, K. Koga and Y. Watanabe. Mater. Sci. Semiconductor Process., 5, 301 (2003).
[2] K. Takenaka, M. Shiratani, M. Takeshita, M. Kita, K. Koga and Y. Watanabe. Pure Appl. Chem., 77, 391 (2005).
[3] H. Kokura, K. Nakamura, I. P. Ghanashev and H. Sugai, Jpn. J. Appl. Phys., 38, 5262 (1999).
[4] V. Schulz-von der Gathen and H.F. Döbele, Plasma Chem. Plasma Process., 16, 461 (1996).
[5] N. Sadeghi, D. W. Setser and M. Touzeau, J. Phys. Chem. A, 106, 8399 (2002).