Influence of the light irradiation on galvanic corrosion of metal gate

D. Watanabe^{1,2}, H. Aoki¹, J.Jong-Hyeon¹, C. Kimura¹ and T. Sugino¹

¹Department of Electrical Electronic and Information Engineering, Osaka University

2-1 Yamadaoka, Suita-Shi, Osaka 565-0871, Japan

Phone: +81-6-6879-7699 Mail: aoki@steem.eei.eng.osaka-u.ac.jp

²Fundamental Research Dept., Chemical Div., Daikin Industries, Ltd.

1-1 Nishi Hitotsuya, Settsu, Osaka 566-8585, Japan

Abstract

Achieving high-performance and low-stand-by power applications requires the integration of new metal gate materials and high-k dielectrics. Wet processes for removing high-k film involve a risk of enhanced galvanic corrosion at the gate electrode level. We have found that the galvanic corrosion of the metal gate in FEOL is remarkably enhanced by the room light irradiation. The interception of light irradiation during the wet processes in FEOL is also required as well as the wet process in BEOL.

Introduction

To achieve high-performance and low-stand by-power applications requires the integration of new metal gate material and high-k dielectrics into LSI devices with the 32 nm technology node and beyond. Recently, many candidate materials such as TiN, Mo and Ru have been investigated for metal gates to address the work function tuning issue in future generation. A diluted HF (DHF) is used for removing residual high-k film (HfSiON) and post-etch residues. Therefore, special chemicals with high selectivity for HfO₂/SiO₂ (Shallow Trench Isolation: STI) have not been required. However, this creates a risk of enhanced galvanic corrosion at the gate electrode during the DHF wet process, as shown in Fig.1. Galvanic corrosion occurs when dissimilar metals come in contact with each other in the solvent. In this case, poly-Si corrodes in the HF solvent, because the electrode potential of poly-Si is smaller than those of TiN, Mo, and Ru.

It is reported that Cu corrosion phenomenon during wet processes in BEOL is enhanced by photo illumination.²⁾ In this work, we investigated the influence of the light irradiation on the galvanic corrosion of the metal gate in FEOL processing.

Experimental

As a model case, we selected Mo as the metal in the stack (work function metal) and doped poly-Si (resistivity $<1\Omega$.cm) for the second material on top (conductor). In the structure of Mo/poly-Si, etching rates of doped poly-Si and galvanic currents were investigated for DHF. The Si wafer and the Mo plate are covered with epoxy resin, leaving two areas exposed on both surfaces as shown in Fig. 2. Anode (poly-Si)/cathode (metal) ratios were fixed at 1:20 in this experiment. The Si corrosion rate on the exposed area was measured after dipping in DHF solutions (0.1wt.%-1wt.%) during illumination by a tungsten-halogen lamp. The galvanic currents between the anode and cathode in DHF were also measured using a potential analyzer. The anode (doped Si wafer)/cathode (Mo plate) area ratio was set to be 1:1 in this experiment.

Results and discussion Fig.3 shows the dependence of Si corrosion rate on the HF concentration in DHF for Mo/doped-Si without irradiation (dark) and with irradiation. The corrosion rate with irradiation drastically increases compared with that without irradiation. The corrosion rate increaes with HF concentration in DHF. Especially, the galvanic corrosion of n-doped Si depends largely on light irradiation compared with that of p-doped-Si. Fig.4 shows the dependence of the corrosion rate of n-type Si on the illumination intensity in DHF (1%). The corrosion rate increases with increasing illumination intensity. The corrosion rate is 3nm/min at even 200lx, which is normal illumination intensity of room light.

Fig.5 shows the polarization curve for the Mo and n-doped Si in the DHF (0.1%) with various illumination intensity. The polarization curves lead the galvanic corrosion current and potential between Mo and n-doped-Si in DHF (0.1%). The corrosion current increases with the illumination intensity. The corrosion rates also exhibit the same dependence as the corrosion current.

Fig.6 shows the dependence of the galvanic corrosion potential between Mo and n-doped-Si on the wavelength of light irradiation in DHF (0.1%). The light source is Xe-lump. The corrosion potential changed in the range of less than 1100nm, which is equal to band gap energy of Si. The result indicated visible spectrum from the room light promote the galvanic corrosion.

Holes in Si substrate induce the galvanic corrosion of silicon, as the following reaction equation, $Si + 4h^+ + 6HF + 4H_2O \rightarrow H_2SiF_6 + 4H_2O + 4H^+$ A lot of holes are generated by the light

irradiation with higher energy than the band gap of Si. Therefore, the galvanic corrosion is clearly dependent on intensity and wavelength of light irradiation. The galvanic corrosion of n-doped-Si is strongly dependent on the light irradiation because an increase of holes is large compared with that of p-doped-Si.

We also investigate the protection of additive surfactant for galvanic corrosion with light irradiation in DHF. It is reported that Si etching in Buffered HF can be suppressed by adsorption of the hydrophobic group with specific surfactants³⁾. Fig.7 shows the galvanic corrosion rate with light irradiation in DHF with surfactants (anion and nonion). However, the galvanic corrosion with light irradiation in DHF can't be suppressed by those additive surfactants.

Conclusion

We have found that the galvanic corrosion in the metal gate in DHF wet process was remarkably enhanced by the light irradiation. The interception of light irradiation during the wet processes in FEOL with metal gate is also required as well as the wet process in BEOL.

References 1) S.Garaud, et.al., Ext. Abs of UCPSS 2006, 113 (2006). 2) Y. Homma, et.al., J.Electrochem,Soc. 147 (2000) 1193.

Fig.1 Galvanic corrosion model of High-k/Metal Gates.

3) Joong S.Jeon, et.al, J, Electrochem, Soc., Vol.142, 2, (1995) 621.





Fig.2 Experimental sample to study the galvanic corrosion of Mo/n-doped Si.



Fig.3 Dependence of Si corrosion rate of (a) Mo/n-doped Si, (b) Mo/p-doped-Si on HF concentration in DHF with and without light irradiation.











Fig.6. Dependence of corrosion potential Mo/n-doped-Si on wavelength in DHF (0.1%) with irradiation and dark.



Fig.7 Corrosion rate with irradiation (1200lx) for DHF with and without surfactants.