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C-2-6

Suppression of Cu oxidation using environmentally friendly inhibitors in the ambience of high temperature and high humidity for Cu/Low-K

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Abstract

Cu surface of via bottom is exposed in the ambience of high temperature and high humidity during annealing after cleaning in via hole of Cu/Low-K. In particular, an environmentally safe inhibitor instead of Benzotriazole (BTA) is required. We have succeeded in an effective suppression of Cu corrosion in the ambience of high temperature and high humidity using environmentally friendly inhibitor (adenine and hypoxanthine).

Introduction

In order to achieve high performance interconnection with small RC delay, the integration of a porous Low-K and Cu wiring is necessary for 32nm-node and beyond LSI devices. After dry etching for damascene formation, wet processes such as cleaning for polymer removal and rinsing with DIW are carried out. Cu surface of via bottom is exposed in the ambience of high temperature and high humidity during annealing after wet processes. (Fig.1) Therefore, the suppression of Cu oxidation and corrosion is a serious problem in wet processes for Cu/porous Low-K interconnections.

On the other hand, BTA has been used as the conventional inhibitor. However, BTA has a large environmental impact because it poorly creates mutagenicity and biodegrades. As environmentally friendly Cu inhibitors to replace BTA, there are several typical natural heterocyclic nitrogen compounds. Fig.2 shows the results of biodegradability examination. We can judge whether biodegradability is good if the nitrogen compound is disintegrated by more than 60% after processing for 14 days. In the N-component heterocycle compounds, adenine and hypoxanthine have high biodegradability of more than 60%. On the other hand, BTA has extremely low biodegradability. [1] In this study, adenine and hypoxanthine are used as Cu corrosion inhibitor.

Experimental

The chemical structures of BTA ($C_6H_5N_3$), adenine ($C_5H_5N_5$) and hypoxanthine ($C_5H_4N_4O$) are shown in Fig.3. The Cu samples were treated with various inhibitors (BTA, adenine, hypoxanthine: 0.1wt% in water, 1min, 25°C) immediately after treatment with oxalic acid (0.1wt%, 1min, 25°C).

These samples were kept for the ambience of high temperature (100°C) and high humidity (100%) an hour. Then XPS measurements were carried out to examine the Cu surface.

Moreover, the desorption temperature of Cu inhibitors was examined by using thermal desorption spectroscopy (TDS).

Results and discussion

Fig.4 shows the XPS spectra of Cu 2p. The Cu-O peak of BTA is clearly observed compared with adenine and hypoxanthine. Fig.5 shows the XPS depth profile of O/Cu ratio on the Cu film. Both adenine and hypoxanthine suppress the oxidation of the Cu surface. All inhibitors suppress the oxidation in Cu bulk.

As the inhibitor film was removed by the first sputtering for XPS observation, it is thought that the film can be easily removed by pre-sputtering before barrier metal deposition.

Fig.6 shows the ratio of Cu-O/Cu signal intensity. It is found that the hypoxanthine treatment can effectively suppress Cu oxidation. Therefore, adenine and hypoxanthine have superior inhibition compared with BTA in the ambience of high temperature and high humidity.

TDS desorption spectra of N (M/z=14) and C-N (M/z=26) which originate in nitrogen were investigated. The large desorption peak for BTA is observed at 330°C as shown in Fig.7(a). In both cases of adenine and hypoxanthine, the large desorption peak is observed around at 420°C (Fig.7(b)(c)). The annealing for water desorption from Low-k film is usually carried out around 350-400°C.

It is difficult for BTA to expect to be an effective inhibition, because the BTA film may desorb during annealing. On the other hand, adenine and hypoxanthine not only have stable inhibition during annealing but also are environmentally friendly inhibitors. It is thought that adenine and hypoxanthine molecules may adsorb approximately horizontally on a Cu surface compared with BTA. Thus, these inhibitors can effectively suppress the oxidation of Cu.

Conclusion

We have achieved an effective suppression of Cu corrosion using environmentally friendly inhibitor (adenine and hypoxanthine) in the ambience of high temperature and high humidity for Cu/Low-K interconnection. Adenine and hypoxanthine are more stable than BTA during annealing. Furthermore, the film can be easily desorbed by pre-sputtering before barrier metal deposition.

This technology can be applicable to 32nm- node and beyond LSI devices.

Acknowledgements

Thanks to ESCO Ltd. for having the TDS measurement.

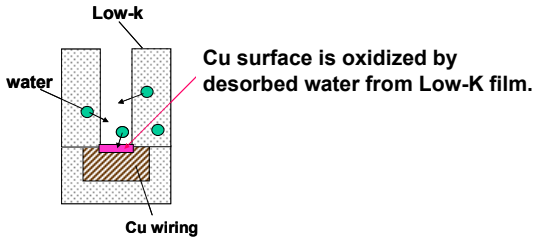

Fig.1 High temperature and high humidity in via during annealing

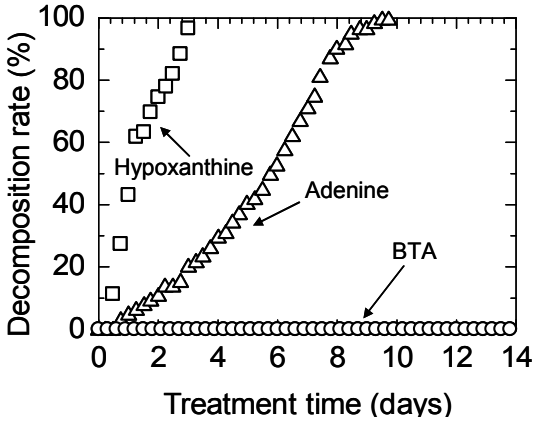

Fig.2 Biodegradation characteristics of BTA, Adenine and Hypoxanthine

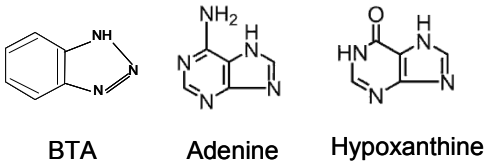

Fig.3 Chemical structure of Cu corrosion inhibitor used in the study

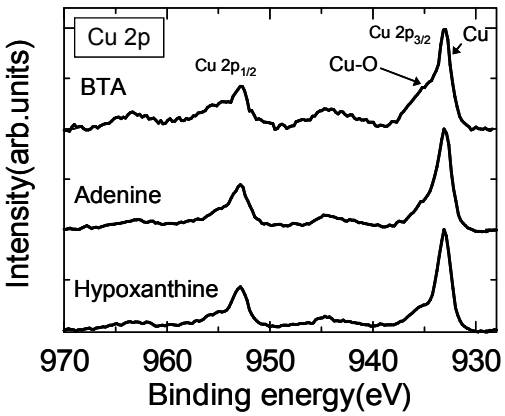

Fig.4 XPS spectra of Cu 2p

References.

[1] T.Koito, K.Hirano, H.Aoki, M.Iji and Y.Kasama, Surface Tech.,Vol. 56 №7(2005) 57.

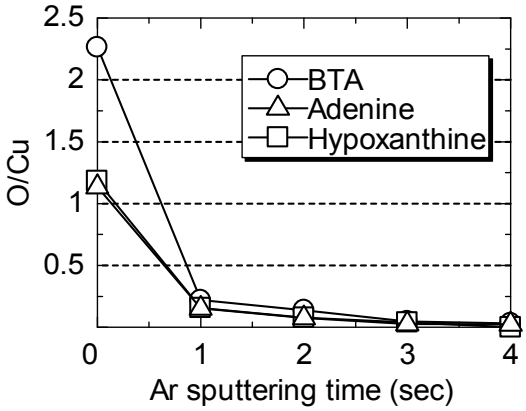

Fig.5 Depth profile of O/Cu in XPS

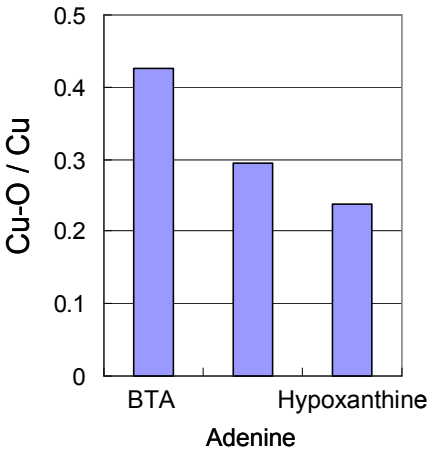

Fig.6 Ratio of Cu-O/Cu signal intensity on XPS

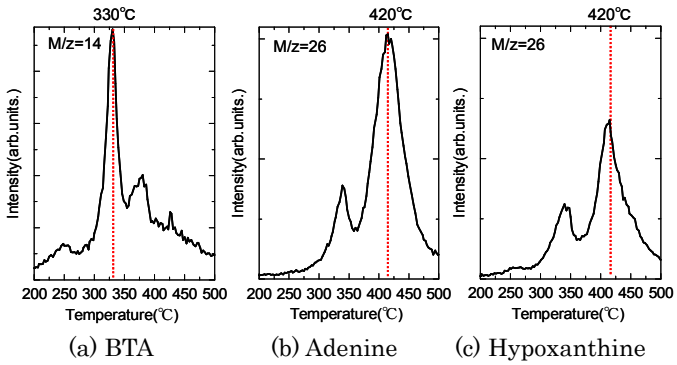

Fig.7 TDS spectra of (a) BTA (b) Adenine and (c) Hypoxanthine