Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp251-252

Smooth Patterning of Ru Film by Electrochemical Etching using Organic based Solution

Lixin Yang[1], Rina Sakae[1], Masaki Yashimaru[2], Mineo Yamaguchi[2], Itaru Kanno[2], MorimitsuTanaka[2], Chiharu Kimura[1] and Hidemitsu Aoki[1]

[1]Dept. of Electrical, Electronic and Information Engineering, Osaka University, 2-1 Yamadaoka, Suita-Shi, Osaka 565-0871, Japan

[2]STARC (The Semiconductor Technology Academic Research Center) 17-2 Shin Yokohama 3-chome, Kohoku-ku, Yokohama, 222-0033, Japan

aoki@steem.eei.eng.osaka-u.ac.jp

Introduction

We have succeeded in etching the Ru (ruthenium) film by electrochemical process using an organic based solution to get smoothly etched area.

Sorts of materials which should be examined are increasing rapidly with enhancing performance of electronic devices and MEMS. For that purpose a new method of etching hard-corroded materials such as noble metals is necessary.

Ru film as one of the candidate barrier material for future BEOL cannot be etched by conventional acidic solutions such as SPM, HPM or conc. HF, and even in aqua regia has no effect. We have reported that the Ru film can be easily etched by electrochemical etching in less than 1% HCl [1)].

This process is useful for Ru removing on wafer bevels/edges. However, in case of Ru patterning, this process has a serious problem that the etched Ru patterns become rough by bubbles generation during etching as shown in Fig.1(b). Based on the pH- potential diagram of Ru, it can be found that there is Ru corrosion area over the oxygen overvoltage line as shown in Fig.2. Therefore, there is a problem of bubbles generation by electrolysis of HCl solution during Ru etching when aqueous solution is used.

In this paper, to avoid the bubbles generation and having smooth etching area, we have proposed an etching of Ru film using electrochemical etching in the organic based solution (IPA: Isopropyl alcohol).

Experiment

Ru (thickness: ~100nm) / SiO_2 / Si substrate was used as an anode electrode (Fig.1(a)). Pt electrode was used as a cathode. Both these two electrodes were immersed in the IPA based solution. The surface of the Ru film was covered with the adhesive resin as a mask. A circle area (diameter: 5mm) was exposed as a reaction area for Ru. For the measurement of corrosion currents, an impedance analyzer was connected with the two electrodes for controlling the applied voltage. Table.1 shows the condition of solutions in this experiment.

Results and discussion

Fig.3(a) and Fig.4(a) show the time dependence of corrosion currents for typical water based HCl solution (HCl: 0.01%) and IPA based HCl solution (HCl: 2.3%), respectively. In case of water based solution, the current drastically decreases towards the endpoint (Fig.3(a)).

In case of water based solution, a very high etching rate is observed as shown in Fig.5. However, only the pattern edge of the reaction area was etched and the etched pattern was very rough by the bubble generation as shown in the surface photograph of Fig. 3(b). Ru film of pattern center is left over by being separated from anode electrode as shown in Fig.1(b), because the edge area with short current pass was preferentially etched.

Meanwhile, the etching rates of organic based HCl solution drastically suppressed compared with that of the water-based HCl solution (Fig.5). On the contrary, the whole reaction area can be smoothly etched as expected as shown in Fig.4(b). In addition, all the Ru film within the reaction area was smoothly etched as shown in the step profile of Fig.6. This means that the solution of IPA based HCl solution can make an ideal result of Ru etching.

Fig.7 shows the XPS depth profile of composition ratio in the Ru films after electrochemical etching. Comparing with the Ru film etched in the water based HCl solution, it is found that oxidation of Ru surface can also be suppressed by IPA based solution.

Conclusion

By electrochemical etching process using organic (IPA) based solution, we have succeeded in smoothly pattering of the Ru (ruthenium) film comparing with the irregular one in case of water based HCl solution. Hence, it is a significant step towards the manufacture of next-generation devices fabrication.

References

[1] H. Aoki, D. Watanabe, N. Ooi, J. Jong-Hyeon, C. Kimura and T. Sugino, Jpn. J. Appl. Phys. 48 (2009) 04C019.

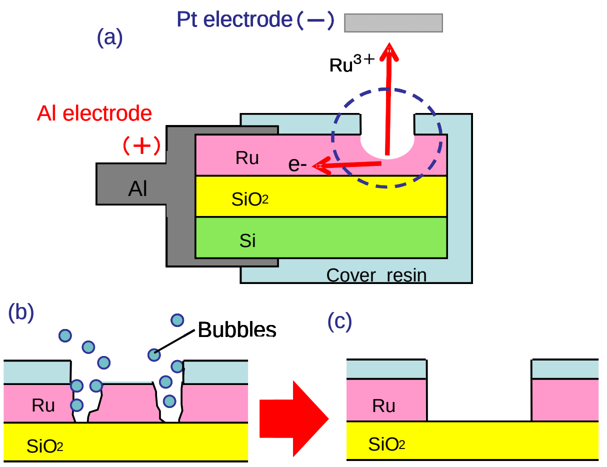

Fig.1 (a) Cross section of Ru sample for this experiment. (b) A conventional etched pattern. (c) An ideal etched pattern.

Table 1 Conditions of solutions in this experiment.

Solution	HCl	H_2O	IPA (Organic solvent)
Water based HCl	0.01% - 0.1%	99.99 – 99.9%	0%
Organic based HCl	0.6% - 2.3%	1.2% - 4.6%	93% - 98.2%

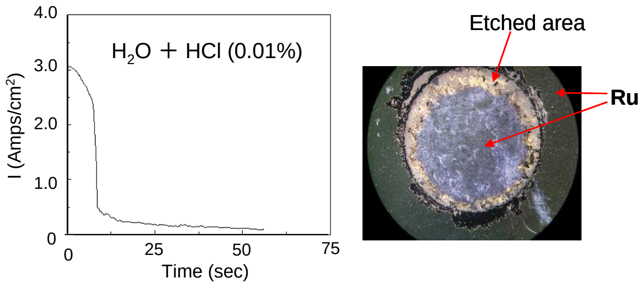

Fig. 3 (a) Time dependence of corrosion currents, (b) etched pattern by water based HCl solution.

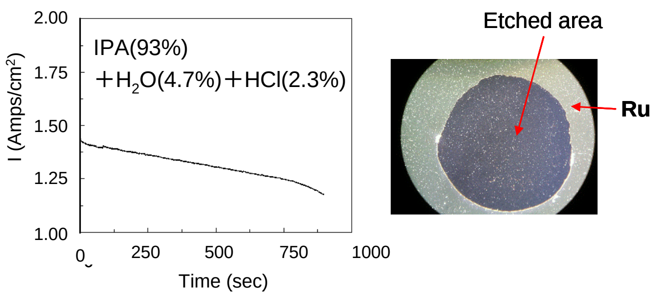

Fig. 4 (a) Time dependence of corrosion currents, and (b) etched pattern by IPA based HCl solution.

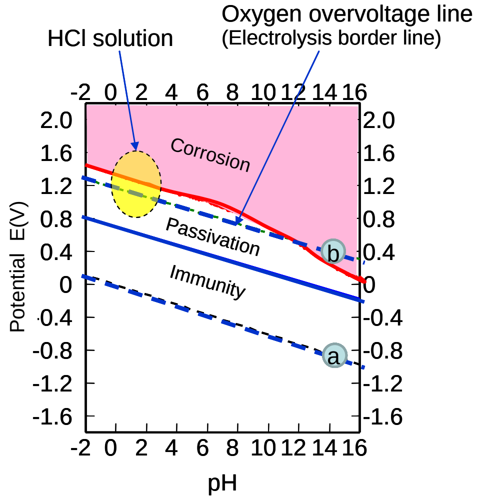

Fig.2 pH-potential diagram of Ru. (Pourbaix Diagram)

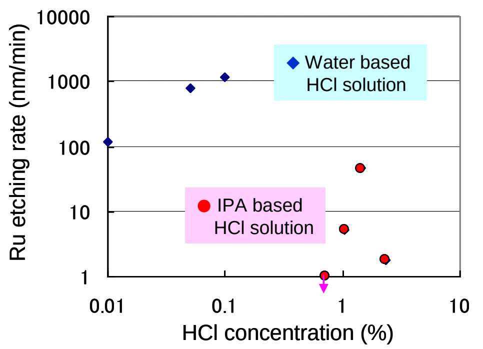

Fig.5 Dependence of Ru etching rates on HCl concentration.

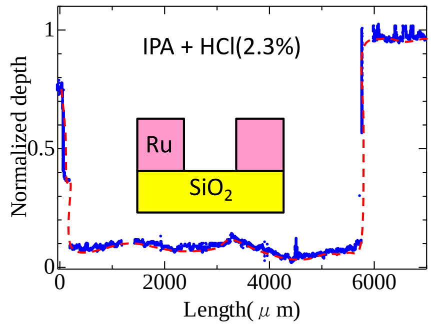

Fig.6 Step profile of the etched pattern.

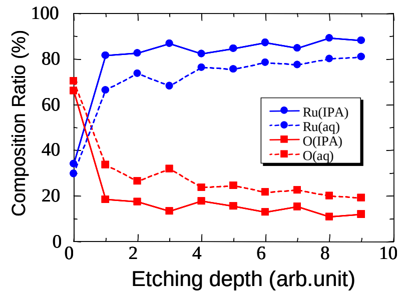

Fig.7 XPS depth profile of composition ratio in the Ru films after electrochemical etching.