SUITABILITY OF N_2 PLASMA FOR THE RIE ETCHING OF THIN Ag LAYERS

P. Hrkút*[1]*, Š. Haščík*[2]*, L. Matay*[1]*, I. Kostič*[1]*,
***A. Benčurová*[1]*, A. Konečníková*[1]*, P. Nemec*[1]*, R. Andok*[1]**

[1] *Inst. of Informatics, Slovak Academy of Sciences, Bratislava, Slovakia*
[2] *Inst. of Electrical Engineering, Slovak Academy of Sciences, Bratislava, Slovakia*

E-mail: Pavol.Hrkut@savba.sk

Received 10 May 2013; accepted 21 May 2013.

1. Introduction

For patterning of thin Ag (and some other metallic) layers the use of H_2, He and Ar as etching gasses has been reported recently [1]. Etching of silver thin films deposited on glass using inductively coupled Cl_2-based plasmas and the effects of various Cl_2-based gas mixtures on the formation of reactive byproducts affecting Ag etching was investigated in [2]. Using of halogen gases for the patterning of Ag layers is not suitable because for the gaseous reactive products of the etching, characterized by their boiling point (b.p.), the temperature is 1159°C for AgF and up to 1550°C for the reactive AgCl product, respectively. More suitable product of the etching seems to be $AgCO_3$ which requires the temperature only 270°C (b.p.); however in the presence of O_2 the resist quickly degrades. The applicability of nitrogen oxide for dry etching of some metals (also Ag) and metallic alloys has been patented in [3]. The most suitable etching gas for our purpose turned out to be N_2 which requires only the temperature of 297°C to create an AgN_3 etching product. We have supposed that during the bombardment of the surface of the silver layer by nitrogen ions (resp. by radicals that are created in nitrogen plasma), these particles would react with the Ag atoms on the surface of the sample and would create AgN_3 products which are subsequently withdrawn by diffusion from the sample's surface.

2. Experimental part

Silver layers of 48nm thickness were evaporated using EB PVD on Si wafers. The masking resist layers were spin-coated and patterned by the EBDW lithography on the ZBA 21 (20keV) (*Carl-Zeiss, Jena*; currently *Vistec, Ltd.*) variable shaped e-beam pattern generator in II SAS. In order to check the etching process in N_2, we covered a part of the samples containing Ag with a layer of various resists. The samples were dried on a hot-plate and RIE etched in SCM 600 (1 Pa; 20 sccm; 500W). After 8 minutes the non-masked Ag layer was completely etched away, what testified suitability of N_2 as an etching gas. Also the etch time of 4 minutes showed to be sufficient for etching through the Ag layer. In order to optimize the etching process it was necessary to estimate the etch-rate (E.R.) of suitable resist layers and of the silver layer. The etch-rates of selected resists are shown in Figure 1.

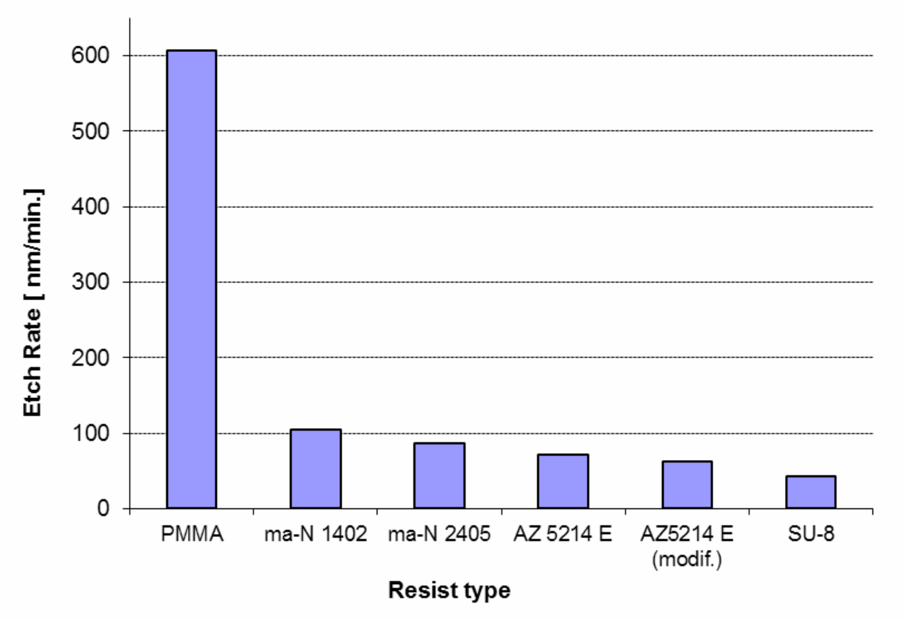

Fig. 1: *Etch rates of selected resists in N_2 plasma.*

We have examined the following resists in N_2 plasma: PMMA (mol. weight 450 000), ma-2405, ma-N 1402 (*Micro Resist Technology, Berlin, Germany*), AZ 5214 E (*MicroChemicals, Ulm, Germany*; also used as image-reversal), and SU-8 2000 (*MicroChem Corp.*), respectively. The following parameters of plasma etching were used: p = 1 Pa, 100-500 W, U_{SB} = -300V. These parameters are summarized in more details in Table 1.

Resist type	rf power [W]	etch time [min]	Intitial resist thickness [nm]	Resist thickness after the etching [nm]	Δ [nm]	etch rate (E.R.) [nm/min]
PMMA	500	1,5	1 000	90	910	607
PMMA	300	3	1 000	400	600	200
PMMA	100	0,7	371	339	32	48
ma-N 1402	500	5	1 900	1 372	528	105
ma-N 2405	500	5	900	465	435	87
AZ 5214 E	500	5	1 300	945	355	71
AZ5214 E (modif. for IR)	500	5	1 100	791	309	62
SU-8	500	5	450	138	212	42

Table 1: *Parameters of RIE etching of selected resists in N_2 plasma.*

As can be seen in Figure 1, the highest E.R. in N_2 plasma was measured for the PMMA resist and the lowest E.R. was found for the SU-8 resist. During the lithography processing of the ma-N 1420 resist we have observed that the used developer D 533S reacts with silver and is thus unusable for this application. For the resist AZ 5214 E, the lithography process was without problems with the commercial developer AZ 726 MIF.

3. Results and Discussion

A) Etching of Ag layers through the PMMA resist

With regard to a high resolution of PMMA we have decided to try this resist in N_2 plasma despite the fact of its high E.R in plasma (Fig. 1; Table 1). We have etched the PMMA (deposited on Ag layers) at different rf power (1 Pa; 20 sccm).

rf power [W]	etch time [min]	Δ [nm]		E.R. [nm/min]		E.R. $_{PMMA/Ag}$ [nm/min]
		PMMA	Ag	PMMA	Ag	
100	10	143	15	14,3	1,5	9,5
150	10	345	26	34,5	2,6	13,2
150	**6**	**121**	**17**	**20,1**	**2,8**	**7,2**
300	6	>1 000	44	>166,6	7,3	>23
300	3	600	15	200	5	40

Table 2: *Parameters of RIE etching of PMMA / Ag layers in N_2 plasma.*

As can be seen in Table 2, optimal etching of Ag layers was achieved at rf power of 150W and the etch-time of 17 min (divided into 3 etch-cycles). For longer etch times increases also the etch rate for PMMA. In other to eliminate the high E.R. of PMMA, we have also used thin a:Si layer as a mask for N_2 RIE plasma and we have observed (also in the case of other examined resists) some silver residuals redeposited on the a:Si surface that emerge at the contours of the structures. The structure of Ag layers on its surface as well as in cross-section was examined in SEM and the size of the grains was measured to be 30-300 nm.

B) Etching of Ag layers through the AZ 5214 E resist

We used standard lithography process for the AZ 5214 E with the AZ 726 MIF developer. The samples were RIE-etched in N_2 plasma (p=1 Pa; P=500W; U_{SB}= -310V; t=4 min). However, the results of the etching also showed there were residuals at the bottom of the etched structures. We have succesfully removed these residuals in O_2 plasma (1 Pa, 300 W,-220V, 4 min) but the silver surface oxidized (blue surface). Further etching in O_2 plasma led to increasing the Ag layer (brown colour); finally, in subsequent N_2 plasma also the Ag oxide was etched away.

C) Etching of Ag layers through the SU-8 resist

The SU-8 resist has been spin-coated on thin Ag layers. The samples were RIE-etched in SCM 600 in N_2 plasma (p=1 Pa; P=500W; U_{SB}= -310V; t=4 min). After the etching, the E.R. for this resist was calculated to be 55 nm/min.

4. Conclusion

The experiments showed that for our e-beam lithography patterning purposes, PMMA is still a good candidate despite the fact that it has the highest etch-rate resistance of all the examined resists. Among other candidates with better plasma resistance, SU-8 and AZ 5214 E are rather suitable, however formation of Ag residuals was observed which are not easy to be removed. In order to use the patterning advantages of PMMA we have sputtered on the surface of Ag (via metallic mask) a thin a:Si layer that served as a mask for RIE etching in N_2 plasma. The resistance the a:Si masking layer in N_2 plasma was very good and an 80nm-thick masking layer was sufficient for etching a 48nm-thick Ag layer. To remove the a:Si masking layer, we have tried SF_6 plasma which turned to be unsuitable due to the fact that sulphur reacts with silver by degrading it. That is why to remove the a:Si layer, CF_4 was used instead as etching gas. The elimination of undesirable Ag clusters after N_2 RIE will be object of our future investigations.

Acknowledgements

The authors would like to thank V. Barák, A. Ritomský and I. Čaplovič (II SAS, Bratislava) for technical assistance in e-beam lithography. This work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic, the Slovak Academy of Sciences No. VEGA- 2/0021/12.

References

[1] Tae-Seop Choi *et al.*, ECS Journal of Solid State Science and Techn. **2**(6), pp. 275-281.
[2] Lee, Young-Joon *et al.*, Japanese Journal of Applied Physics **42**,1 (2003), pp. 286.
[3] I. Nakatani, *Dry etching*. US patent No. 6878635 B1.