

THE AZ 5214E RESIST IN EBDW LITHOGRAPHY AND ITS USE AS A RIE ETCH–MASK IN ETCHING THIN AG LAYERS IN N₂ PLASMA

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In this article we describe the electron-beam direct-write (EBDW) lithography process for the AZ 5214E photoresist which is, besides its sensitivity to UV radiation, sensitive also to electrons. An adapted process flow is provided. At the same time we examine the resistance of this resist to RIE and its suitability as an etch-mask for etching thin Ag layers in N₂ plasma. A comparison with several chosen resists (PMMA, ma-2405, ma-N 1402, SU-8 2000) is provided.

Keywords: AZ 5214E resist, PMMA resist, image reversal, EBDW lithography, characteristic curves, RIE, etch-rates

1 INTRODUCTION

Coming out from observations that some positive ultraviolet (UV) resists are e-beam sensitive and behave like photosensitive resists, we have fixed on one of such resist representatives, namely on the commercial AZ 5214E photoresist manufactured by *Clariant Corp.* (Switzerland). This resist is a mixture of solid and liquid substances ($\sim 72\%$; containing nominally 0.5% of water). Its solid constituents are formed by a novolac (phenol-formaldehyde polymer resin) and a diazonaphthoquinone (DNQ) photoactive compound; the latter blended into the novolac polymer matrix, enabling the dissolution of the novolac matrix in aqueous base solutions if irradiated or non-irradiated by UV light (resp. by electrons). The main liquid constituent in AZ 5214E is the propylene glycol monomethyl ether-1,2-acetate (PGMEA) solvent [1].

According to its Product Data Sheet, AZ 5214E shows besides its sensitivity to UV radiation, also sensitivity to irradiation by electrons. Recently several articles have been published with regard to the mentioned resist; let us mention some concerning the resist's deposition technique [2, 3, 7], e-beam proximity effect corrections and diffusion in the photoresist [4], the resist's mechanism and evaluation [5], as planarizing and bridging material [6, 7], some applications [5, 9], *etc.*

The AZ 5214E photoresist is normally intended for lift-off techniques which call for a negative wall profile. Although it is a positive photoresist comprised of a novolac resin and DNQ as photoactive compound (PAC), it is mostly used in the image reversal (IR) mode also for its excellent dry etch resistance and thermal stability. The PAC is consumed during the exposure and once fully exposed, the resist will not any longer contain unreacted PAC. The resist's IR capability is obtained by a special

crosslinking agent which becomes active at temperatures above 110°C and only in the exposed areas of the resist [1]. The crosslinking agent together with exposed PAC lead to an almost insoluble (in developer) and no longer light sensitive substance, while the unexposed areas still behave like a normal unexposed positive photoresist. After a maskless flood exposure, the overall result is a negative image of the mask pattern with a negative wall profile ideally suited for lift-off. The principle of reversal baking with the AZ 5214E resist is well described in [5]. With variations to the basic image reversal scheme and without much increase in chemical count, one may fine-tune lithography recipes to suit particular needs. An example of how the scheme can be applied to a practical lift-off lithography can be found for instance in [9].

The AZ 5214E has been reported also as a suitable masking resist for the RIE etching [10]. For patterning of thin Ag (and some other metallic) layers the use of H₂, He and Ar as etching gasses has been described in [11]. Etching of silver thin films deposited on glass using inductively coupled Cl₂-based plasmas and the effects of various Cl₂-based gas mixtures on the formation of reactive byproducts affecting Ag etching was investigated, *eg.* in [12]. 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 AgCO₃ which requires the temperature of only 270°C (b.p.); however in the presence of oxygen the resist quickly degrades. The applicability of nitrogen oxide for dry etching of some metals (also Ag) and metallic alloys has been patented in [13]. The most suitable etching gas for our purpose turned out to be N₂ which requires only the temperature

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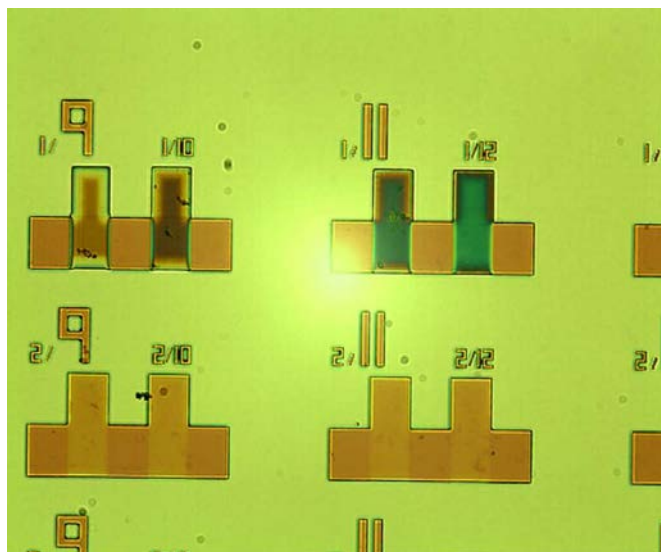


Fig. 1. Example of an EW test with under-, over- and normally-exposed areas, respectively

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

The EBDW lithography experiments have been carried out on ZBA 21 (20 kV) and ZBA 23 (40 kV mode, LaB_6 cathode) variable shaped e-beam pattern generators (Carl Zeiss, Jena; currently Vistec, Ltd.) at II SAS. We have used the so called Exposure Wedge (EW) test that serves for the construction of the sensitivity (characteristic) curve and for extracting the contrast γ value of the resist for optimized resist pre- and post-exposure process parameters. We obtained the dependency of the remaining resist thickness to the applied exposition dose within large-area exposures (Fig. 1). We have exposed series of EW test samples (deposited on Si as well as on GaAs substrates) with exposure doses ranging from 10 to $640 \mu\text{C}/\text{cm}^2$. Our experiments showed that the AZ 5214E resist is electron sensitive and further in the text we show its technological process flow that suited our technological needs.

In order to obtain ca 400 nm film thickness at 5500 rpm spin-speed, we used diluted solution of AZ 5214E (1:1, by the AZ EBR Solvent). We adjusted the following resist process flow for the AZ 5214E in IR mode useful for the EBDW patterning: standard resist spin-coating; pre-bake at 120 °C/120 s on hotplate (HP); EBDW lithography (ZBA23 at 40 kV, 50 nm mode); post-bake at 115-130 °C/2 min with a step of 5 °C (for technology fine-tuning); UV maskless exposure (Karl Süss) for 15 s (this step turns the resist to IR); resist development in

AZ400K + H_2O (1:5) for 1 min; final rinse in H_2O for 10 s.

Figure 2 shows normalized resist thickness dependence as a function of exposure dose for four different post-bake temperatures ranging from 115 to 130 °C, step 5 °C (for 2 min at hot-plate). Silicon wafers were used as substrates. As the most critical parameter of the IR process is the reversal-bake temperature, it was kept constant within ± 1 °C to maintain a consistent process [1]. This temperature was optimised individually. Finally we considered 125 °C to be the optimal post-bake temperature for our process, which is in good agreement with the results indicated in [5]. The measurements on EW tests were carried out using the standard profilometry technique (Talystep, Alphastep).

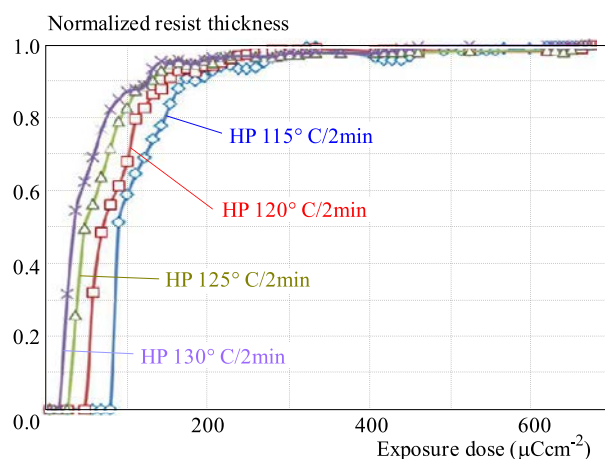


Fig. 2. Characteristic curves for the AZ 5214E resist (in IR mode) on Si at 40 kV accelerating voltage

For the RIE experiments, Ag layers of 48 nm thickness were evaporated on Si wafers using EB PVD technique. The masking resist layers were spin-coated and patterned

Table 1. RIE parameters for N₂ plasma of selected resists

Resist type	RF power (W)	etch time (min)	Intitial resist thickness (nm)	Resist thickness after the etching (nm)	Δ (nm)	etch rate (ER) (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 (mod. for IR)	500	5	1 100	791	309	62
SU-8	500	5	450	138	212	42

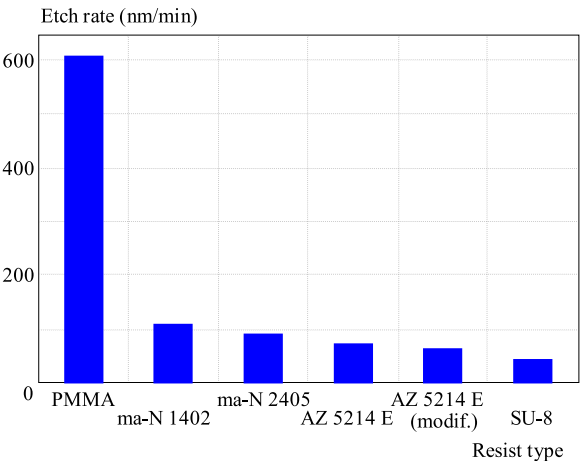


Fig. 3. Etch rates of selected resists in N₂ plasma

by the EBDW lithography on the ZBA 21 (20 keV) variable shaped e-beam pattern generator. In order to check the etching process in N₂ plasma, a part of the samples containing Ag was covered with a layer of various resists. The samples were dried on a hot-plate and RIE etched in SCM 600 (1 Pa; 20 sccm; 500 W). After 8 minutes the

non-masked Ag layer was completely etched away, what testified the suitability of N₂ 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 the resist layers and of the silver layer. The etch-rates of selected resists are shown in Fig. 3.

The following resists were etched in N₂ plasma: PMMA (mol. weight 450 000), ma-2405, ma-N 1402 (*Micro Resist Technology, Berlin, Germany*), AZ 5214 E (*MicroChemicals, Ulm, Germany*; also used in IR mode), and SU-8 2000 (*MicroChem Corp.*), respectively. The parameters of plasma etching (with $p = 1$ Pa, RF in the range 100–500 W, $U_{SB} = -300$ V) are summarized in more details in Table 1.

As can be seen in Fig. 1, from the examined resists, the highest E.R. in N₂ plasma was found for the PMMA resist and the lowest E.R. was obtained for the SU-8 resist (the value only slightly less than that of AZ 5214E). 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 our purposes. For the AZ 5214E resist, the lithography process was without problems when the commercial developer AZ 726 MIF was used.

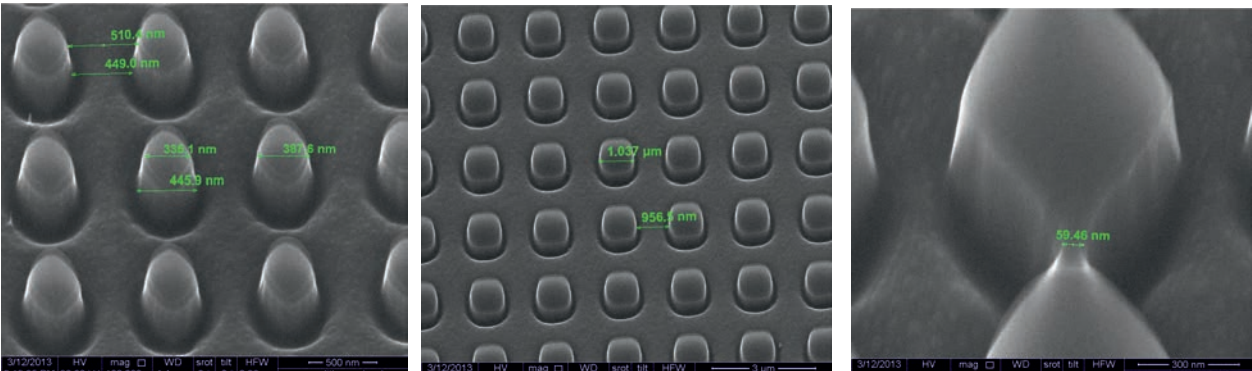


Fig. 4. SEM pictures of patterns achieved with the AZ 5214E, used at the same time as an etch mask for etching GaAs in SiCl₄ plasma. Left: an array of dots (450/450 nm); middle: an array of dots (1/1 μm); right: detail of a 60 nm narrow motive created by this process.

Table 2. RIE parameters for PMMA/Ag layers in N₂ plasma

RF power (W)	etch time (min)	Δ (nm)		ER (nm/min)		ERPMMA/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	> 1000	44	> 166.6	7.3	> 23
300	3	600	15	200	5	40

3 RESULTS AND DISCUSSION

AZ 5214E used in EBDW and as an etch mask in SiCl₄ plasma

Figure 4 shows patterns on GaAs wafers exposed in the AZ 5214E resist by EBDW, followed by the RIE process with the resist used as a masking layer. To prevent resist charging during the e-beam exposure, the samples were covered by a thin layer of chromium (12 nm), which was subsequently removed by standard wet chemical etching.

SEM pictures of patterns were achieved with the AZ 5214E, used at the same time as an etch mask for etching GaAs in SiCl₄ plasma. Left: an array of dots (450/450 nm); middle: an array of dots (1/1 μ m); right: detail of a 60 nm narrow motive created by this process.

An array of 450/450 nm dots is shown (Fig. 4) with visible layer of masking AZ 5214E on top of the structures (removed in later step). To achieve this profile three different exposure doses were used, after the exposure of the patterns the samples were descummed in O₂ plasma (150 W, 1 Pa, 30 s) and subsequently RIE etched in SiCl₄ plasma (40 W, 2 Pa, 3 min). A rather good homogeneity of the dots across the wafer was achieved; however an effect of trenching can be seen in the neighbourhood of the etched patterns. Due to a good resistance of the AZ 5214E resist to SiCl₄ etching, we exposed the samples to another etching in oxygen plasma in order to decrease the resist thickness and its opening.

RIE of Ag layers through the PMMA

With regard to a high resolution of PMMA (better than that of the examined AZ 5214) we have decided to try this resist in N₂ plasma despite the fact of its high E.R. value (Fig. 3; Tab. 1). We have etched the PMMA (deposited on Ag layers) at different RF power (1 Pa; 20 sccm).

As can be seen in Table 2, optimal etching of Ag layers was achieved at RF power of 150 W and with the etch-time of 17 minutes (divided into 3 etch-cycles). For longer etch times increases also the etch rate for the PMMA. In order to eliminate the high E.R. of PMMA, we have also used an a:Si layer as a mask for N₂ 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 in the range of 30 to 300 nm.

RIE of Ag layers through the AZ 5214E

We used standard lithography process for the AZ 5214E with the AZ 726 MIF developer. The samples were RIE-etched in N₂ plasma ($p = 1$ Pa; $P = 500$ W; $U_{SB} = -310$ V; $t = 4$ min). However, the results of the etching showed also that there were residuals at the bottom of the etched structures. We have successfully removed these residuals in O₂ plasma (1 Pa, 300 W, -220 V, 4 min) but the silver surface oxidized (blue surface). Further etching in O₂ plasma led to increasing the Ag layer (brownish colour); finally, in subsequent N₂ plasma also the Ag oxide was etched away.

4 CONCLUSIONS

We have described an EBDW lithography process for the AZ 5214E photoresist which was used in image-reversal mode for its good properties for lift-off. Besides its rather good e-beam patternig use, this resist has shown to be interesting also for its resistance towards etching in N₂ plasma (to etch thin Ag layers) but also in other plasmas (SiCl₄, CCl₄ and SF₆). An array of 450/450 nm dots of a good homogeneity across the wafer was achieved by a technique described in the article.

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 5214E are rather suitable, however formation of Ag residuals during RIE was observed which are not easy to be removed. In order to use better patterning advantages of PMMA and the above mentioned advantages of AZ 5214E, 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 N₂ plasma. The resistance the a:Si masking layer in N₂ plasma was very good and an 80nm-thick masking layer was sufficient for etching a 48 nm-thick Ag layer. To remove the a:Si masking layer, we have tried SF₆ 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.

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