Thick PhotoResist Outgassing During MeV Implantation

(Mechanism & Impact on Production)

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Abstract - The generation of an ion beam and its impact into photoresist-masked wafers will have an adverse effect on the vacuum of an MeV ion implanter. This is particularly significant when implanting with higher energies and higher beam current through the thick photoresist.

In this paper, we will present the mechanism and effects of photoresist outgassing caused by high energy ion implantation (250KeV to 3 MeV). Due to photoresist outgassing and its effects, production usable beam current on small process chamber can be significantly limited. Photoresist outgassing from various implant conditions will be discussed. Photoresist of various thicknesses up to 4.5um from several vendors and both positive and negative acting resists were compared. Both ionization (electron stripping) and neutralization (electron addition) were measured as dose shift (underdose or overdose) using TW and Rs analysis. Depending on the ion species, energy and beam current, chamber pressure rises. The pressure rise could be as high as in the E-4 torr range. If the chamber pressure is kept below 3.0E-5 torr no observable dose shift could be detected.

I. INTRODUCTION

For many years, a number of applications requiring high energy ions for implantation of semiconductor devices have been developed. These applications include the following: formation of retrograde wells and conventional well structures in sub-half micron CMOS technology[1,2]; formation of buried layers in both MOS and bipolar devices[3]; late programming of memory and logic[3]. These applications require ions with energies ranging from approximately 200KeV to several MeV and doses ranging from 1.0E12 to about 5.0E14 ions/cm^2.

The use of high energy ions introduces new challenges for masking materials. The extended range of the projectiles in photoresist requires masks which are several microns thick. With higher energy implants in the thick photoresist, outgassing in the process chamber must be examined to minimize errors in dosimetry resulting from pressure increases.

In this paper, we will present the mechanism and effects of photoresist outgassing caused by high energy ion implantation. Photoresist outgassing with various implant conditions will be discussed. Photoresist of various thicknesses up to 4.5µm from several vendors and both positive and negative acting resists are compared. Both ionization (electron stripping) and neutralization (electron addition) were measured as dose shift (underdose or overdose) using TW and Rs analysis. Depending on the ion species, energy and beam current, chamber pressure rises. The pressure rise could be as high as in the E-4 torr range. If the chamber pressure was kept below 3.0E-5 torr no observable dose shift could be detected.

II. EXPERIMENTAL TECHNIQUES

A. Sample preparation

The implant conditions and type of resist used in this study are shown in Tables I and II respectively. High energy B and P implants into thick photoresist wafers were performed using a Genus G1520 high energy ion implanter. Both 150 and 200 mm wafers were used in this study.

The JSR ix-405EM (Positive) & NFR-012R (Negative) samples were prepared by JSR at their Sunnyvale, CA facility. The samples were prepared as follows. The coating was applied on a SVG coater followed by a soft bake at 90°C, 60sec for ix-405EM positive resist and 90°C, 120sec for NFR-021R negative resist. The film thickness achieved was 2.5 and 4.5um respectively. Using a Nikon 1755i7A stepper the samples were then exposed followed by a post bake at 120°C, 60sec for ix-405EM and 90°C, 60sec for NFR-021R. The development process was for 60sec at single puddle. The Shipley samples were prepared at OPTO-Line, Wilmington, MA. The coating was done on a Headway 101 coater with 2000 R.P.M for 30 sec followed by 90°C, 30min softbake in a Blue-m convection oven.

B. Measurements

Endstation vacuum measurements were performed using a Genus G1520 high energy ion implanter. During the implants, the pressure was monitored by the ion gauge in the endstation to obtain a measure of the total gas evolved

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from the resist during ion bombardment. After the implantation, each wafer was measured for dose shift using Therma-Wave intensity and the wafers were then annealed at 960°C, 30min with N_2 ambient for sheet resistance measurement using a Prometrix Omni-map 4-point probe. From these data, a determination of photoresist outgassing and dosimetry shift could be made.

Table I Implant Conditions

Species	*Energy (KeV)*	*Dose (ion/cm²)*	*Beam I (pμA)*
Phos	500	3.0e13	50~200
	1000	4.0e13	50~500
	2000	3.0e13	50~200
Boron	2000	3.0e13	50~200

Table II Photoresist Summary

P/R	*Type*	*Thickness (μm)*	*Pretreatment before implant*
Shipley S1400-31	Positive	4.0	SB:95°C,30min
JSR ix-405EM	Positive	2.5	SB: 90°C,60s PEB:120°C, 60s
JSR ix-405EM	Positive	4.5	SB: 90°C,60s PEB:120°C, 60s
JSR NFR-012R	Negative	4.5	SB: 90°C,60s PEB:120°C, 60s

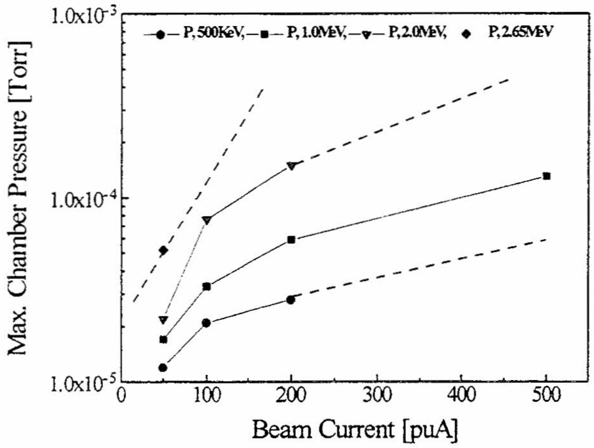

Fig. 1. Photoresist Outgassing : Max. Endstation vacuum pressure as a function of beam current.

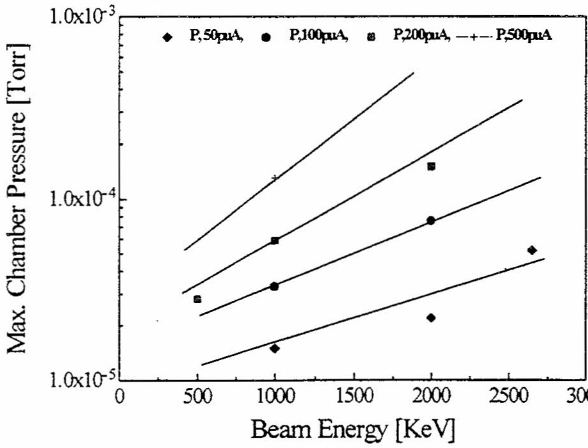

Fig. 2. Photoresist outgassing : Max. Endstation vacuum pressure as a function of implant energy.

III. Results and Discussion

A. Photoresist outgassing - Implant Condition

From previous reports on photoresist outgassing mechanism, it was noted that outgassing is not caused by thermal effects[4]. Figs. 1 and 2 show the pressure variation measured in the endstation as a function of beam current and energies for Phos implants into Shipley S1400-31 positive PR. It can readily be observed that photoresist outgassing increases dramatically with beam current and energy level. In this case, the pressure in the endstation is proportional to the beam power in the beam as shown in Fig. 3, but this is not due to wafer heating. The first factor is proportional to beam current and the second factor is proportional to ion energy. It is clearly shown that the endstation pressure has a stronger dependence on the implant energy. The endstation pressure increases dramatically with increase of energy (>1.0MeV) and easily reaches the 1.0E-4 torr range.

B. Effect of P/R outgassing on dose shift

The dose will be affected if this reaction occurs as shown in Fig. 4. This result indicated that there is a very strong relationship between dose shift in sheet resistivity and endstation vacuum degree. If the chamber pressure is kept below 3.0E-5 torr, no significant dose shift was observed in the large process chamber. The increase in chamber pressure for the small process chamber results in unacceptable dose errors due to small volume and poor pumping performance. As shown in Fig. 5, measurement of the endstation vacuum pressure during the implantation with 1.0MeV phosphorus ions agreed reasonably well with the results of Fig. 4.

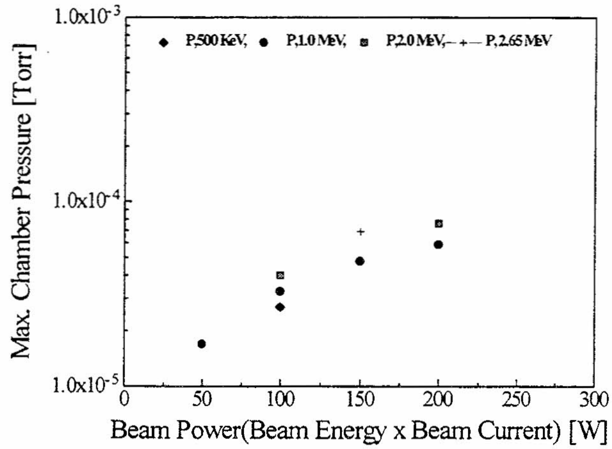

Fig. 3. Photoresist outgassing : Max. Endstation vacuum pressure as a function of beam power.

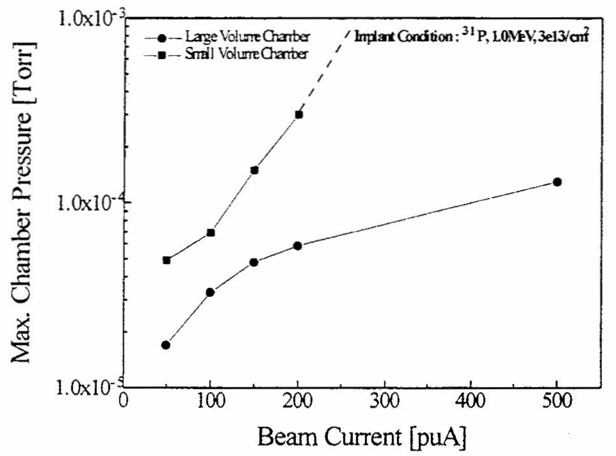

Fig. 5. Photoresist outgassing : Max. Endstation vacuum pressure with various chamber volume.

C. Photoresist outgassing - Photoresist

Since photoresist outgassing is a major issue for MeV implantation, the evaluation of photoresist outgassing was done for the different specific formulations of photoresists made by various manufacturer. Table III shows a comparison of outgassing of JSR ix-405EM positive resist and JSR NFR-012R negative resist. In both cases, the most prominent species of the total outgassing was hydrogen (neutralization). Only 12 to 20% of the endstation chamber pressure difference was observed between negative resist and positive resist with Phos. implantation. In Table IV, other studies were performed for boron implantation. In this case, 2.5μm positive resist shows only 8% of the endstation chamber pressure difference compared to the 4.5 μm positive resist.

Table III Effect of resist on vacuum pressure (Positive vs. Negative)

Resist	*Type*	*Thickness (μm)*	*Pressure (torr)*	*ΔP*
Implant Condition : ^{31}P, 2.5MeV, 3.0e13/cm^2 I_B=70puA				
JSR ix-405EM	Positive	4.5	9.6e-5	1.00
JSR NFR-012R	Negative	4.5	8.5e-5	0.88
Implant Condition : ^{31}P, 2.0MeV, 3.0e13/cm^2 I_B=200puA				
JSR ix-405EM	Positive	4.5	2.0e-4	1.00
JSR NFR-012R	Negative	4.5	1.8e-4	0.80

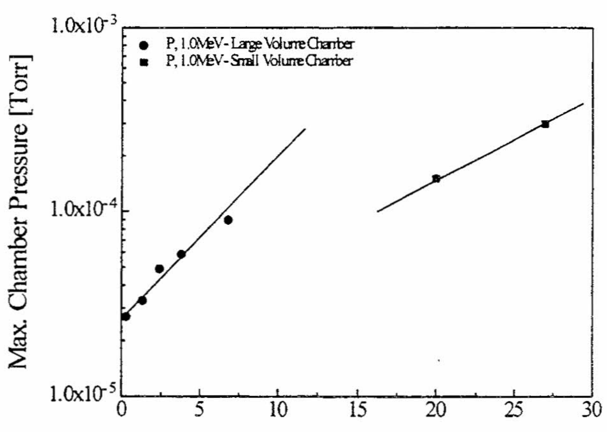

Fig. 4. Relationship between shift in Sheet Resistivity and endstation vacuum degree

These studies showed that the amount of outgassing observed did not change significantly when a different resist type and various resist thicknesses were employed.

One of the consequences of photoresist outgassing, or the increased pressure in the endstation and beamline portions of the implanter is a partial neutralization and/or ionization of the ion beam in the vacuum system. These undesirable charge exchange mechanisms can cause errors in measuring the beam current, and therefore cause errors of overdosing as well as underdosing of the wafer in high energy machine. As shown in Table V, when the chamber pressure exceeds >3.0E-5 torr, a dose shift is observed as either overdose (Neutralization) or underdose (Ionization) on different photoresist made by various manufacturers. These results indicate that the dose shift due to neutralization or ionization is a function of photoresist material content, pretreatment and history. Therefore, as a result, this effect is not accurately predictable.

Table IV Effect of P/R Thickness & Type on vacuum pressure

Resist	*Type*	*Thickness (μm)*	*Pressure (torr)*	*ΔP*
Implant Condition : ^{11}B, 2.0MeV, 3.0e13/cm^2 I_B=100puA				
JSR ix-404EM	Positive	2.5	6.5e-5	0.92
JSR ix-405EM	Positive	4.5	7.0e-5	1.00

Table V Dose Shift - Ionization vs. Neutralization

Resist	*Implant (Phos)*	*Pressure (torr)*	*R_S (PR/Bare)*	*Dose Shift*
JSR	2.5MeV,3e13	9.6e-5	396 / 406	Neutralization
TOK	1.0MeV,1e13	4.1e-5	840 / 815	Ionization
Shipley	Multi Implant	5.7e-5	356 / 346	Ionization

IV. SUMMARY AND CONCLUSION

The following were observed.

(1) Photoresist outgassing increases dramatically with beam current and energy level. The endstation pressure increases rapidly with increase of energy (>1.0MeV) at the beam current of >100pμA and easily reaches the 1.0E-4 torr range.

(2) In the high energy implantation case, the pressure in the endstation is proportional to the beam power in the beam, but this is not due to wafer heating.

(3) When the chamber pressure exceeds >3.0E-5 torr, a dose shift is observed. The increase in chamber pressure for small process chamber results in unacceptable dose errors due to the small volume and poor pumping performance.

(4) Only a 12 to 20% endstation chamber pressure difference was observed between negative resist and positive resist. 2.5μm thick photo resist shows only an 8% difference in the endstation chamber pressure compared to the 4.5μm thick photo resist. These results showed that the amount of outgassing observed did not change significantly when a different resist type and various resist thicknesses were employed.

(5) When the chamber pressure exceeds >3.0E-5 torr, a dose shift is observed as either overdose (Neutralization) or underdose (Ionization) on different photoresist made by various manufactures. These results indicate that dose shift due to neutralization or ionization is a function of photoresist material content, pretreatment and history. Therefore, as a result, this effect is not accurately predictable.

(6) Due to photoresist outgassing and its effects, the amount of usable beam current on small volume chamber can be significantly limited.

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