Minimizing the outgassing of spin-coated organic materials to reduce defects

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ABSTRACT

Maintaining low-defect spin-applied films is paramount to the success of semiconductor manufacturing. While some spin-on films have a low number of defects as coated, defect levels can rise with the number of wafers processed. Thin organic films may outgas or sublime during the post-coat baking process, or even during subsequent exposures to deep or extreme ultraviolet radiation. If these outgassing components collect on the lid of the hot plate chamber, there is an increased risk of "fall-on" defects on subsequently processed wafers. To increase throughput, preventive maintenance and cleaning schedules are pushed to the limit to provide maximum output from the track. New materials must be designed to produce minimal outgassing to ensure maximum throughput without defects. Early tests for measuring outgassing provided qualitative results gained from collecting the condensed outgassing components on a quartz wafer and measuring the absorbance of the resulting film. A more advanced technique involves the use of a newly designed quartz crystal microbalance (QCM) to more carefully quantify the amount of outgassing.[1] As the industry continues to mature, more sensitive measurements are required to design new materials with even lower outgassing from sublimation. The combination of QCM and inverted wafer test provides an overall view of total outgassing and ramifications of the outgassing being produced.

Keywords: Sublimation, outgassing, QCM, defects, BARC, spin-on coatings

1. INTRODUCTION

Maintaining low-defect spin-applied films is paramount to the success of semiconductor manufacturing. Significant effort has been placed on reducing defects of spin-on applied films by making improvements to material formulations, application processes, and application equipment. A primary requirement for spin-on films is to have a low number of defects as coated. Without a substantially defect-free coating, yield, and thus profits, will be reduced. An often-overlooked problem in early screening of materials is the outgassing effects on defect levels. Thin, organic films may outgas or sublime during the post-coat baking process, or even during subsequent exposures to deep or extreme ultraviolet radiation. If these outgassing components collect on the lid of the hot plate chamber, there is an increased risk of fall-on defects on subsequently processed wafers whereby defect levels can rise with the number of wafers processed between cleaning of the collection surface. Cleaning the collection surface alleviates this problem. To increase throughput, preventive maintenance and cleaning schedules are pushed to the limit to provide maximum output from the track. New materials must be designed to produce minimal outgassing to ensure maximum throughput without defects.

Early tests for measuring outgassing provided qualitative results gained from collecting the condensed outgassing components on a quartz wafer and measuring the absorbance of the resulting film. A more advanced technique involves the use of a newly designed quartz crystal microbalance (QCM) to more carefully quantify the amount of outgassing.[1,2] As the industry continues to mature, more sensitive measurements are required to design new materials with even lower outgassing. Materials that form extremely thin coatings necessarily contain a high percentage of solvent and other volatile components that would be difficult to remove completely while retaining desired film properties. However, not all outgassing collects and forms particles on a surface that can render a fall-on defect. To ensure a reduction in fall-on defects without the convolution of benign evaporation, a combination of testing is required.

Described in this paper is the use of a next-generation tool for QCM testing for the development of low-subliming coatings in conjunction with inverted wafer testing to relate the total outgassing collection of solid particulate material on a surface above the wafer while undergoing a baking process. Key formulation factors for sublimation performance were identified. Then a base formulation was prepared; this variation

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provided the best correlation between chemical composition and outgassing. In this manner, outgassing effects were studied independent of lithography performance or other variables.

2. METHODOLOGY

2.1 Materials

An acrylic polymer was synthesized to serve as a model of the base resin component in BARC-type materials. The model polymer was made with equal molar fractions of a methacrylate with pendant hydroxyl groups and methylmethacrylate. This polymer functions as a good model system because many of the BARC polymers used to date throughout the industry are based on the acrylate backbone and contain a hydroxy unit for a crosslinking site. The methylmethacrylate was used in place of any other monomers needed to complete the performance or optic parameters of the BARC resin and helps in the solubility of the polymer in the model solvent system. Two industry common aminoplast crosslinkers were used and are based on glycouril and melamine. Three different curing catalysts were chosen for the model system and are all common sulfonic acids. The selected solvent system models those typically used in the industry, propylene glycol methyl ether (PGME) and propylene glycol methyl ether acetate (PGMEA). The ratio of the components was chosen to represent a formulation typical of BARC technology, but with a higher loading of components compared to the average to reduce the number of wafers needed to see particle generation on inverted wafers (Table I). With a simple yet representative model system, contributions from each type of component could be determined.

Table I. Sample composition of the polymer, crosslinkers, and catalysts used in the testing. A solvent ratio of 60:40 of PGME:PGMEA was used for all samples. Total percent solids were 4% with a component mass ratio of 1:0.25:0.03 polymer:crosslinker:catalyst for all samples.

Name	Crosslinker	Catalyst
Sample 1	Glycouril	1
Sample 2	Glycouril	2
Sample 3	Glycouril	3
Sample 4	Melamine	1
Sample 5	Melamine	2
Sample 6	Melamine	3

2.2 Equipment & procedures

2.2.1 QCM

The QCM (Fig. 1) was developed for the purpose of determining the sublimation of samples of BARC and other spin-on coating products. The quartz crystal was suspended over a hot plate where it could collect the outgassing from the wafer below. A ventilation line was attached at the top to draw airflow upwards and allow the outgassing to condense on the surface of the quartz crystal. The condensate collected on the crystal, and the change in resonant frequency was corrected to mass units of the condensate. The standard process for measurement includes a 4-inch silicon wafer coated with an organic spin-on coating. The wafer was then placed under the QCM on a hot plate at 205°C for 120 seconds. The data were collected and graphed to show sublimate versus time.

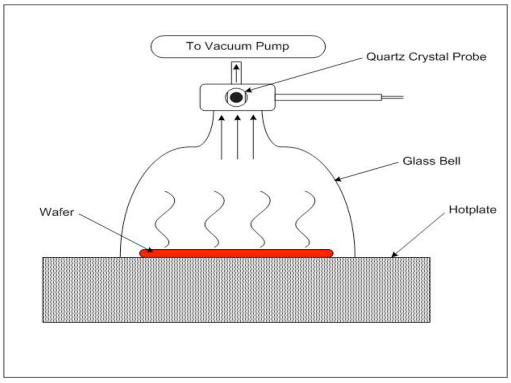

Fig. 1. Diagram showing the QCM apparatus on a hot plate.

2.2.2 TEL® Clean Track® Mark 8

The TEL® Clean Track® Mark 8 is a 200-mm wafer processing tool with various modules used to apply, bake, and develop spin-on coatings. A modified bake module held a blank inverted wafer above the coated wafer and heating surface to collect subliming materials (Fig. 2). Wafers coated with the model organic spin-on materials of Table I were processed in the modified bake module at 205°C for 60 seconds. The hot plate ventilation was reduced to zero to accelerate the collection of material. The blank inverted wafer was removed and measured on a defect detection tool.

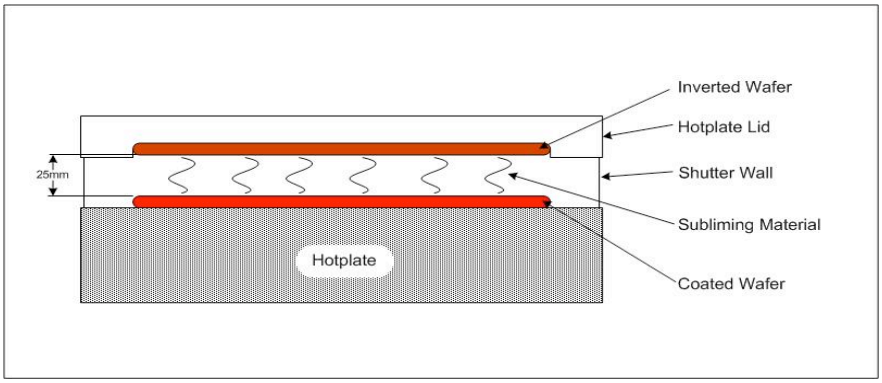

Fig. 2. Diagram of the inverted wafer apparatus installed in the TEL Clean Track Mark 8.

2.2.3 KLA-Tencor® Candela™ CS20 tool

The KLA-Tencor® Candela CS20 is a dark field defect detection tool capable of measuring defects as small as 80 nanometers. The inverted wafer from the TEL® Mark 8 was measured using a specular detector to search for defects collected during the baking process. Data points were collected after 10, 20, 25, and 30 wafers were processed through the modified hot plate holding the inverted wafer. A 20-millimeter edge exclusion was used to eliminate any transfer defects produced when the wafer was inserted and removed from the modified hot plate. Defects sizes ranging from 0.2 µm to > 1.5 µm were measured.

3. DATA AND RESULTS

Figs. 3 through 8 and Table II are a compilation of the testing data. Figs. 3 and 4 show the amounts of sublimate produced over time by the formulations containing glycouril and melamine, respectively, for samples containing each of three different catalysts. Fig. 5 compares the total amount of sublimate produced by the glycouril and melamine formulations containing the three different catalysts. Fig. 6 shows the accumulation of defects for sample 2 as the number of processed wafers increased. Table II shows the defect count for all six samples after 20 wafers were processed beneath the inverted wafer. Fig. 7 shows the total particles for each of the six samples after 20 wafers were processed. Fig. 8 shows scanning electron microscope (SEM) micrographs of large particle defects from inverted wafers.

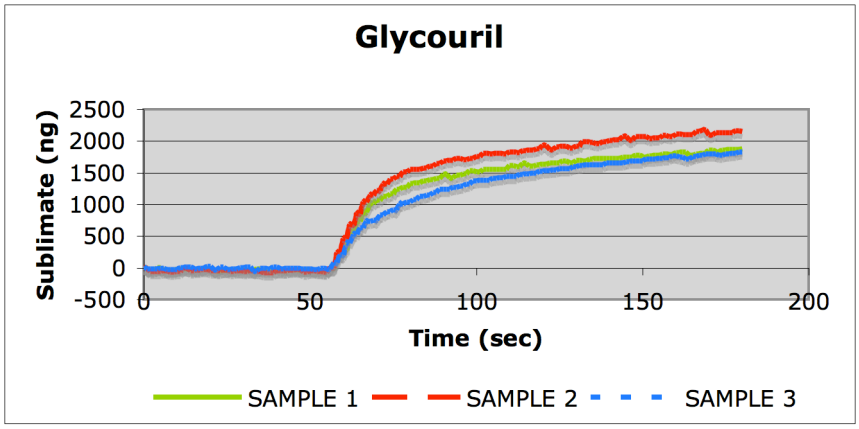

Fig. 3. The polymer with crosslinker glycouril combined with three different catalysts. The QCM graph above shows the total amount of sublimate that was produced from the three combinations.

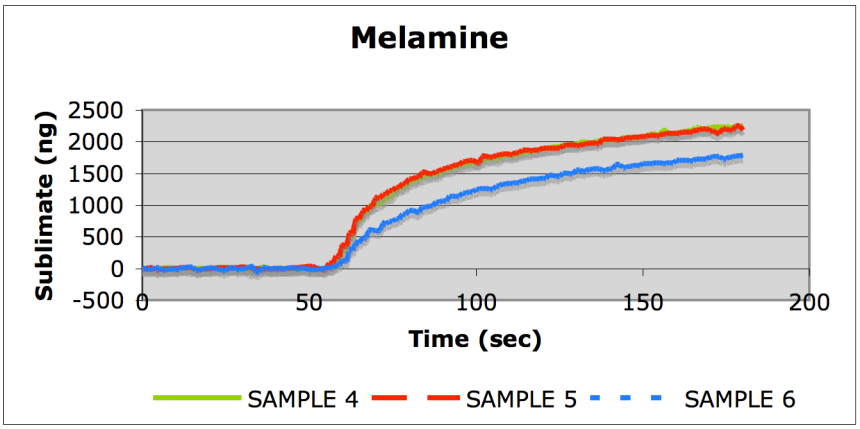

Fig. 4. The polymer with the crosslinker melamine combined with the three different catalysts. The QCM graph above shows the total amount of sublimate that was produced from the three combinations.

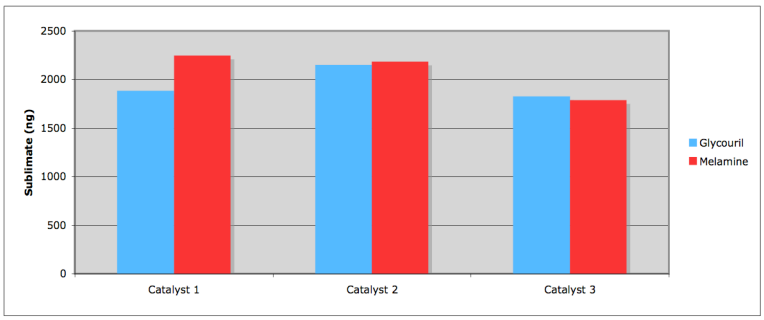

Fig. 5. Comparison of the total sublimate between glycouril and melamine using three different sulfonic catalysts.

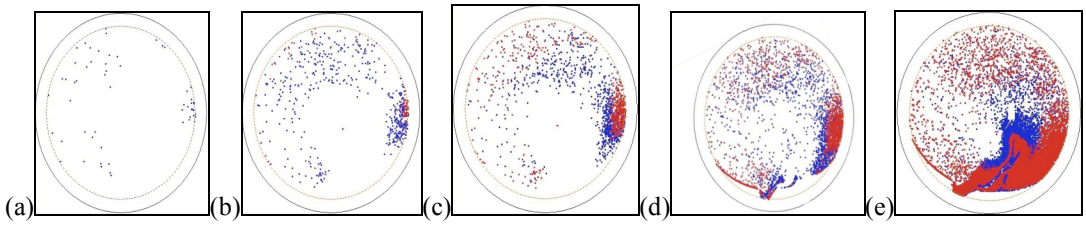

Fig. 6. Progression of the particle defect accumulation of sample 2 after (a) 10, (b) 15, (c) 20, (d) 25, and (e) 30 wafers processed beneath the inverted wafer.

Table II. Defect count total after 20 wafers were processed beneath the inverted wafer.

Crosslinker		**Glycouril**			**Melamine**		
Sample Name	**Blank**	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Total Defects	7	1,256	1,443	14	60,585	1,412	258,729

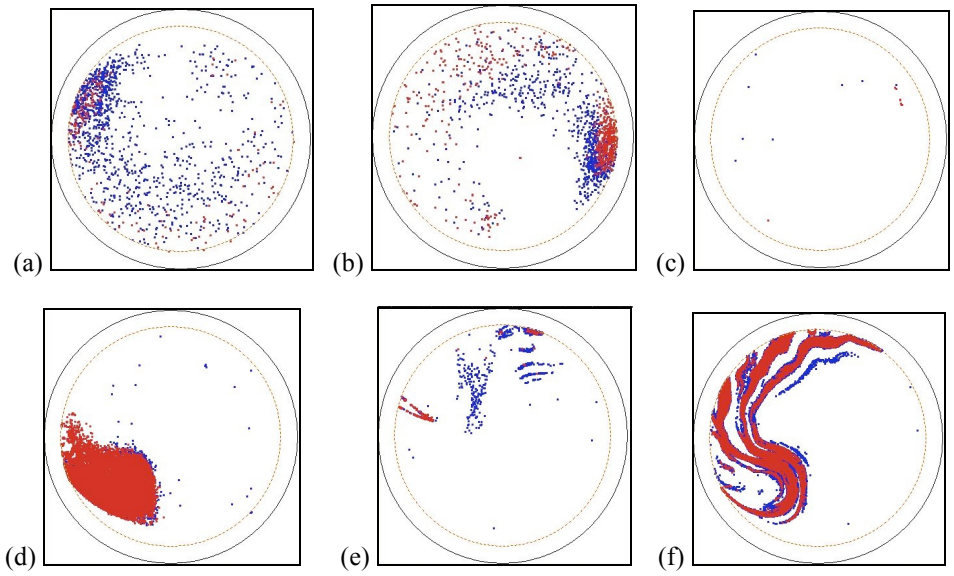

Fig. 7. Total defect count of inverted wafers of (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, and (f) sample 6 after 20 wafers were processed beneath.

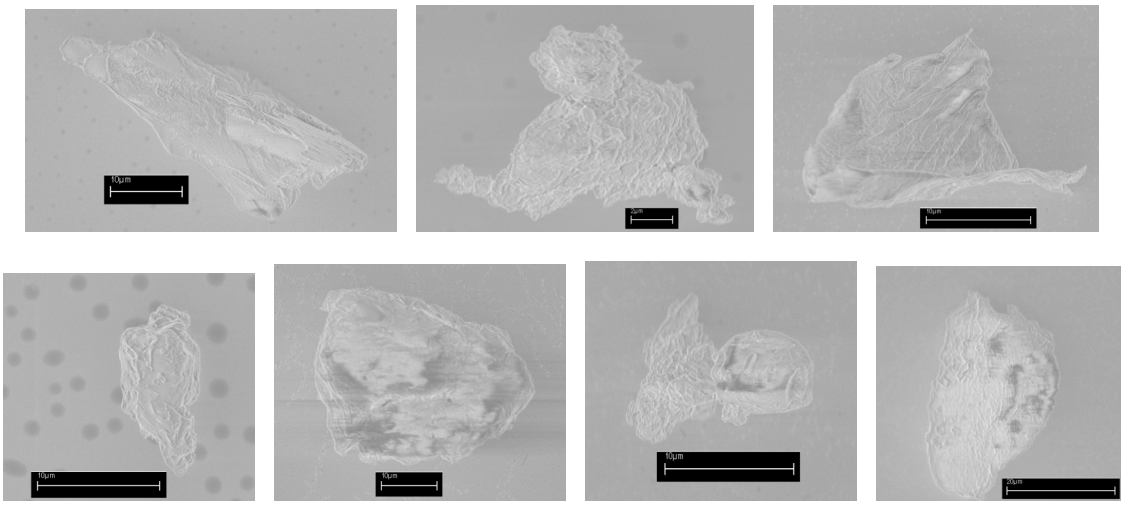

Fig. 8. A collection of SEM micrographs of large particle defects from inverted wafers.

4. DISCUSSION

The QCM graph in Fig. 3 shows that the total output of outgassing of catalyst 1 and catalyst 3 was approximately 1800 nanograms of sublimate each, whereas catalyst 2 sublimed at a higher rate to produce 2200 nanograms of sublimate. In Fig. 4, catalyst 1 and catalyst 2 sublimed at higher rates to produce 2200 nanograms each compared again to catalyst 3, which produced 1800 nanograms of sublimate. Catalyst 3 performed the best with both crosslinker formulations. Catalyst 2 was similar in maintaining a higher sublimation rate for both crosslinkers. Catalyst 1 exhibited an interesting difference between the crosslinkers. Combined with glycouril, catalyst 1 produced outgassing comparable to that of catalyst 3. Combined with melamine, catalyst 1 produced a higher amount of outgassing comparable to that of catalyst 2. The QCM is mass sensitive and cannot distinguish between a residue, a partial film, or large particles. The quartz crystal measures only the material that has adhered to the surface of the crystal. The QCM cannot distinguish among polymer, crosslinker, PAG, TAG, quencher, and/or solvent system outgassing; it measures only the total collection of the mass condensed. The QCM system helps in the first line of detection of possible future problems by helping to keep the outgassing of new formulations at reasonable levels.

The inverted wafer test results demonstrate the sublimate growth over time as coated wafers pass through the bake unit. To establish the noise threshold for the test, the number defects added to the wafer by placing it in and removing it multiple times from the bake unit had to be determined. A defect-grade wafer was inserted into the bake unit lid, allowed to thermally equilibrate, removed, placed in a wafer cassette, and scanned on the defect detection tool for five cycles, which established the threshold at +3 defects. The defect detection method used the specular detector. This limited the minimum detectable defect size to 0.2 µm. It took only a few wafers processed in the accelerated conditions before large enough defects were detectable on the specular scanning procedure. Fig. 6 shows the added defects as the baking process progressed. Clearly the lack of airflow to the ventilation system has allowed for the acceleration of particle formation and to a detectable size. Table II demonstrates that differentiation of the samples can clearly be seen. These data do not include particles that are smaller than 0.2 µm or continuous films produced on the wafers. Inspection of these defects shows actual particle formations shown in Fig. 8. If any of these particles would subsequently dislodge and fall onto wafers below, the result would be fall-on defects.

The QCM is indiscriminate in detection of the specific outgassing components of a particular material. Overall reduction in sublimate is beneficial in material product design. Not all outgassing creates particles that produce fall-on defects, as demonstrated by sample 3 in Table II. Inverted wafer testing provides a better picture of actual fall-on defect potential.

5. CONCLUSION

Due to the differences between QCM testing and inverted wafer testing, their results are more complimentary then comparative. Product development and testing should not be constrained to one or the other type of testing. We demonstrated that particle generation on an inverted wafer does not correlate with the mass accumulation on the QCM crystal. Samples with the same total mass produce significantly different particle counts on the inverted wafer. Developing products that produce low sublimation as measured by QCM is a necessary stage of product development, but not significantly sensitive enough to qualify a product. The inverted wafer testing demands more resources and should be used in the development of materials that demonstrate low total outgassing.

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