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Corporate Responsibility: A Green Initiative to Reduce Chlorobenzene Based Chemistries in Semiconductor Processing

Monique J. Farrell[1], Kevin Frey[1], John Mason[1]

[1]*Northrop Grumman Corporation, PO Box 1521, Baltimore, MD, USA*

ABSTRACT

Climate change and an increase in endangered species, are examples of technological advances negatively impacting the environment. As technology demands increase, an earnest effort to reduce the environmental impact of processing and manufacturing related activities is critical. From a business perspective, minimizing or removing toxic process chemicals is a high impact area that can increase work environment safety and decrease waste management costs. This work presents processing considerations when transitioning to greener alternative polymer resist solvents, for applications in nanomanufacturing with sustainability considerations. Within government contracting, process modifications that change product form, fit, or function require qualification and at minimum justification. This work presents the conversion from a chlorobenzene to anisole based solvent using a 495 kMW polymetheyl methacrylate polymer resin, without impacting form fit or function of the intended device. Resist conversion is of interest as the difference in the substituents of the two solvents, impact the effective toxicity of the polymer resists. Specifically, the oral median lethal dose (LD_{50}) in rats for chlorobenzene is 1110 mg/kg, while anisole is 3700 mg/kg. Therefore, developing a process utilizing anisole and replacing chlorobenzene addresses safety concerns and contributes to green initiatives worldwide. Within this work electron beam lithography fabricated transistor components consisting of a double layered source, and gate were converted from a chlorobenzene to anisole based process; while maintaining process of record specifications. The purpose of this work is to provide a starting platform for individuals seeking to convert from a chlorobenzene solvent to an anisole based resist for sub-micron lithography steps.

INTRODUCTION

Advances in semiconductor processing facilitate the production of increasingly smaller devices, effectively growing the number of transistors that fit on a single chip [1, 2]. New technologies that push the physical limits of Moore's law continue to progress, decreasing transistor footprints [3]. Unfortunately, many of these processes use toxic and unsustainable chemicals including potential carcinogens, strong acids/bases, as well as harsh organic solvents. Therefore a simultaneous approach to advance processing capabilities and technologies, must be coupled with earnest efforts to reduce the impacts of processing and manufacturing related activities on the environment and human operators [4]. This work highlights the need for multifaceted and comprehensive process improvements. Improvements which are not limited to production yield, but expand to encompass exploration and implementation of greener processes reducing the use of toxic chemistries in semiconductor processing [5-7]. Reduction and replacement of these chemistries with alternative

processes can increase work and environment safety, while decreasing waste management costs [8]. This work presents processing considerations when transitioning to greener alternative polymer resist solvents, for applications in nanomanufacturing with sustainability considerations. When evaluating these changes, considering quality and statistical process control concepts are critical to building support for a green initiative based project. In addition, strategies to comprehensively evaluate potential impact to product form, fit, or function are discussed. This work focuses on the conversion of the current process of record (POR) which uses a 495 kMW polymetheyl methacrylate (PMMA) resin suspended in chlorobenzene to an anisole based solvent without impacting form fit or function of the intended device. Resist conversion from chlorobenzene to anisole is of interest as several occupational studies have shown evidence of induced inflammation, respiratory issues and other negative impacts on health while using chlorobenzene based chemistries [9]. The National Institute for Occupational Safety and Health (NIOSH) describes the effects of short term exposure as irritating to the eyes and skin, with the potential to cause chemical pneumonitis if swallowed and aspirated into the lungs [10]. The NIOSH also provides statements of caution related to potential impacts on the central nervous system, resulting in lowering of consciousness. Long term exposure of chlorobenzene includes defatting of the skin, and negative effects on liver and kidney functions. Although the NIOSH also comments on irritation to eye and skin, defatting, and risk of pneumonitis if swallowed for anisole, the risk of central nervous system impact and main organ function concerns are not mentioned [11]. In addition, the FDA categorizes anisole and isopropanol as class three chemicals, whereas chlorobenzene is defined as a class two chemical, similar to chloroform [12]. A class three chemical is considered less toxic and of lower risk to human health, while a class two chemical should be limited in use. The use of anisole as an alternative resist is not new, however this work presents a systematic approach to converting a resist process under the strict requirements of government contracting mission and quality assurance guidelines. This approach is combined with a lean and statistical process control perspective that enables strong support and commitment from management and lead engineers. Within this work electron beam lithography fabricated transistor components consisting of a double layered source and gate, were converted from a chlorobenzene to anisole based resist process; while maintaining process of record specifications. This work provides a starting platform for individuals seeking to convert from a chlorobenzene solvent to an anisole based resist for sub-micron lithography steps. It is important to note, due to the sensitive nature of the technologies funded under government contacts, exact processing details were removed to prevent replication of the device. Again, this work serves as a potential blueprint to evaluate and implement resist conversions for processes which use chlorobenzene based resist chemistries [13].

EXPERIMENTAL DETAILS

Materials

Chemicals purchased were obtained and used without additional purification or filtering from manufacturer. Isopropanol alcohol was procured from KMG electronic chemicals. A 98.5% purity methyl isobutyl ketone was purchased from Puritan. All polymer resists were purchased from MicroChem.

Methods

Instrumentation: The 8600 SVG-RITE track coating system was used to spin coat each polymer resist onto a three inch silicon test or device substrate. A standard dynamic dispense and subsequent bake was then employed. Resist thickness and uniformity were determined using a Nanometrics Nanospec-2. A Leica 5000+ electron beam system by Leica microsystems was used to expose the generated patterns. Lithography derived structures were imaged using an 8250xp critical dimension scanning electron microscope (CDSEM) by KLA–Tencore, and an Amray SEM model 3600FE. **Expose:** The generated patterns were fractured using the same base parameters utilized in the process of record. Example standardized parameters include beam step size, resolution, trapezium distance, and grid size. Between runs, all differences in the beam mode parameters were negligible and were attributed to common variations within the fine focus, and current settings. Before exposure, a standard manual global alignment was executed followed by fine wafer alignment using square marks. In addition, all wafer trials were exposed using a high tension voltage of 50keV. Exposure dose variation was achieved using the layout beam software to create pattern dose gradients across the wafer. Doses ranged from 420 uC/cm^2 to 580 uC/cm^2. **Develop:** The methyl isobutyl ketone and isopropanol (MIBK:IPA) developer solutions were prepared using a graduated

cylinder and allowed to stabilize for a minimum of twelve hours. All wafers were developed in a total volume of 1400 ml of developer solution and rinsed in IPA to stop the develop process.

DISCUSSION

Identify Alternative Resist

When converting any process of record it is important to first define all critical to quality characteristics of the product or process step. This is often accomplished with a critical to quality diagram (Figure 1). To assist in scoping the project, a general need statement should be agreed upon with all key stakeholders. For example, this can include representatives from management, programs, process engineering/integration, and quality. In Figure 1 the need is defined as an anisole based process specification to fabricate the ohmic contact lithography steps for the double source, and gate templates, replacing the chlorobenzene process of record. The need statement is often general and hard to measure, therefore identifying the drivers that will impact the success of the statement is necessary. The drivers of this new process include producing nominal lithography, metal deposition and process capability/stability. The exact methods or parameters required to accomplish the drivers should be discussed and recorded under the critical to quality characteristics (CTQ's) section.

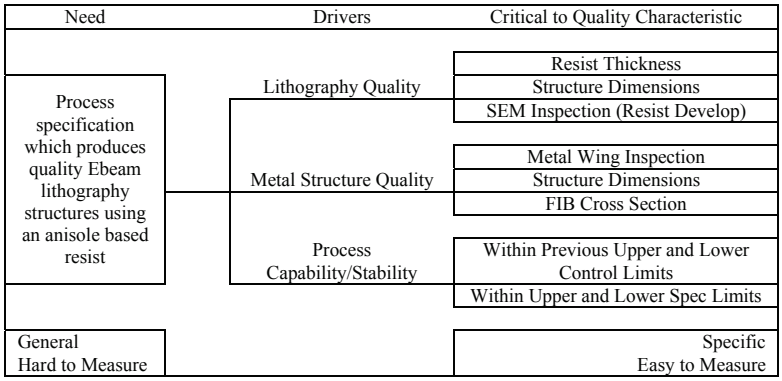

Figure 1: Sample critical to quality diagram assessment of proposed process.

When designing a new process, it is beneficial to review the current process inputs and outputs, clarifying in-use methods to evaluate product or step quality. Often this information will be recorded in a process specification document and statistical process control chart, detailing information such as the process parameter targets, average, spread, control limits and spec limits. For example, the lithography template quality is defined by the achieved critical dimension averages and uniformity. During the process conversion evaluation, the structure linewidth, POR inspection and historical process capability and stability were compared to predict behaviour of new process. Comprehensively filling out the critical to quality diagram is important to define the potential parameters of the new process and desired outputs. The CTQ diagram exercise defined the targeted resist thicknesses for each Ebeam step and scoped the next step of process development. The current process utilizes a 495PMMA C6 resist, in a double coat process. To optimize the transition from chlorobenzene to anisole, a single coat process in conjunction with the resist change was explored. A literature search was completed to down select potential anisole based resist options capable of producing the desired coat thicknesses. It is recommended to source technical information regarding products from the intended manufacturer of purchase. For this process, projected lower limit and upper limit achievable resist thicknesses were estimated and summarized within the table below based on MicroChem spin speed curves (Figure 2, Table 1).

Table 1: Projected resist thickness lower limit and upper limit values based on spin speed curves provided by MicroChem.

MW (kg/mol)	% PMMA in Anisole	Resist Thickness Lower Limit (μm)	Resist Thickness Upper Limit (μm)
495	A2	0.05	0.1
495	A4	0.175	0.3
495	A6	0.325	0.6
495	A8	0.5	1.0
495	A11	1.1	2.25

Combining this information with the target resist thicknesses from the process of record, the top three resist options were purchased and tested in-house; 495PMMA A9, 495PMMA A10, and 495PMMA A11. After cross referencing the target resist thicknesses of each Ebeam level with the spin speed curves in Figure 2, 495PMMA A11 was chosen. It is important to note that the 495PMMA A10 resist also produced target thicknesses. However, the 495PMMA A11 was chosen as it provided a centred process which did not require excessively fast or slow spin speeds to maintain target thicknesses. Creating a new process which can accommodate common cause and special cause variation is important for robust processing, and should be considered when choosing materials and process parameters.

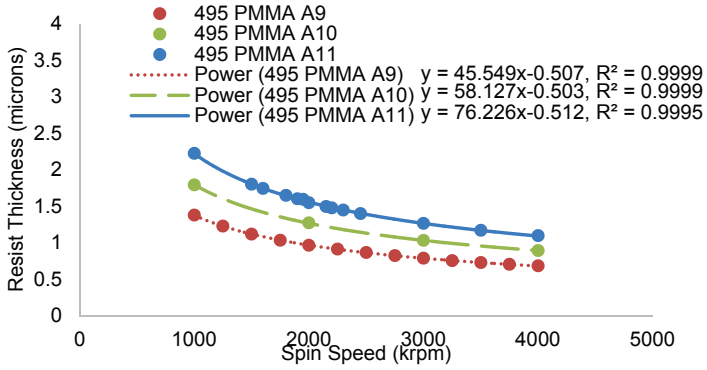

Figure 2: Experimental spin speed curves using 495PMMA A9, 495PMMA A10, and 495PMMA A11.

Ebeam Exposure Optimization

After coat step optimization, the Ebeam exposure parameters were determined. A dose array centred on the POR dose, ranging from 420 uC/cm^2 to 580 uC/cm^2 was applied to test wafers coated with the anisole resist. The structure linewidths at each specific dose were obtained using the CDSEM and graphed as a function of the applied dose. In Figure 3, the electron beam exposure dose arrays for each respective Ebeam level is displayed. The ohmic contact to the source and ohmic contact to the thick source curves can be described with a linear regression and an R^2 value greater than 0.98 (Figure 3A). The change in gate linewidth as a function of dose can also be discussed using a linear regression (Figure 3B). Based on the curves in Figure 3, three doses producing the target linewidths based on POR specifications were chosen. Modulating the dose or develop time is a standard technique to retarget or re-centre the lithography process. Ensuring your

linewidth as a function of dose or develop time can be described with a high confidence interval regression, is key for controlling the process in the future.

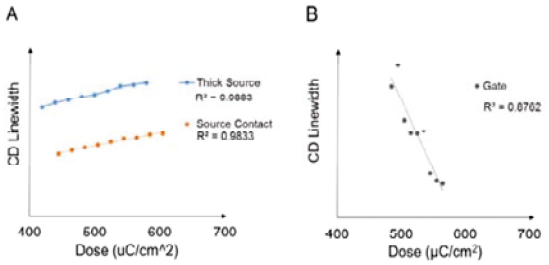

Figure 3: Electron Beam exposure dose arrays for each respective EBeam level. A) Ohmic Contact to the Source, and Ohmic Contact to the Thick Source. B) Ohmic Contact to the Gate.

Single Wafer Exposure Uniformity

Process capability and stability of the new process was preliminary evaluated using Figure 4. Over ninety structures for each EBeam level were measured and plotted on a statistical process control (SPC) chart (Figures 4 A, C, and E). All measured data points were within the control and spec limits of the previous process. In addition, visual observation of the resist from a top down perspective was evaluated and passed standard inspection (Figures 4 B, D, and F). Verifying the predictability of a newly designed process is imperative to understanding the process window and ensuring the new process is adequately resistant to fluctuations.

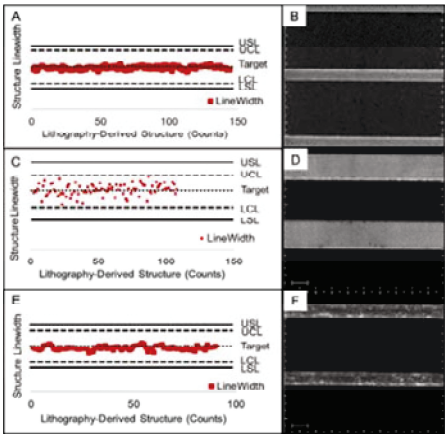

Figure 4: Statistical process control chart of lithography structure dimensions. A) Ohmic Contact to the Source. C) Ohmic Contact to the Gate. E) Ohmic Contact to the Thick Source. Scanning electron microscopy images of lithography structures. B) Ohmic Contact to the Source. D) Ohmic Contact to the Gate. F) Ohmic Contact to the Thick Source.

Post-Lithography Processing Evaluation

To facilitate and optimize process integration, monitoring process outputs post the intended process change module is key to understanding potential impact on subsequent processing steps. Figure 5 displays the SEM images of post-lithography processing through metallization and lift off steps, for a chlorobenzene and an anisole based resist lithography. Figure 5A (chlorobenzene), and figure 5B

(anisole) provide a visual of the achieved ohmic contacts to the source, indicating no appreciable difference between the two processes. In addition Figures 5C and 5D also highlight the congruency between the two gate processes, using either chlorobenzene or anisole as the resist solvent.

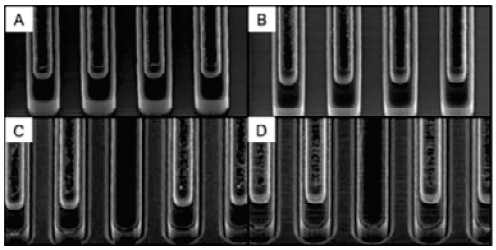

Figure 5: Scanning electron microscopy images of post-lithography processing. Ohmic Contact to the Source: A) Chlorobenzene and B) Anisole. Ohmic Contact to the Gate: C) Chlorobenzene and D) Anisole.

CONCLUSIONS

The authors would like to encourage scientists and engineers who work with chemical solvents and materials to evaluate their current processes with the intention of reducing or removing toxic chemistries. A proactive and earnest effort in this initiative has the potential to minimize the environmental impact of processing and manufacturing related activities, increasing work environment safety and decreasing waste management costs. This work presents processing considerations when transitioning to greener alternative polymer resist solvents, for applications in nanomanufacturing with sustainability considerations. Within this work electron beam lithography fabricated transistor components consisting of a double layered source and gate, were converted from a chlorobenzene to anisole based process; while maintaining process of record specifications. The purpose of this work is to provide a starting platform for individuals seeking to convert from a chlorobenzene solvent to an anisole resist based resist for sub-micron lithography steps. Future work will centre on developing anisole coat and expose procedures to replace remaining processes including: metalized brick gate/T-gate structures and device channel etch processes.

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