The deep ultraviolet spectroscopic properties of a next-generation photoresist

Application Note

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Abstract
The deep UV spectroscopic properties of a next-generation photoresist material have been investigated using a Cary Deep UV spectrophotometer equipped with a ‘VW’ specular reflectance accessory. Measurements were made in a nitrogen-purged glovebox. The photoresist was spin-coated onto a silicon wafer 10 cm in diameter, and was characterized over the wavelength range 150 to 250 nm. The data obtained illustrates the homogeneity of the photoresist investigated, and further demonstrates the ability of the Cary Deep UV spectrophotometer to acquire high quality reflectance spectra in the deep UV region.

Introduction
Chemically amplified photoresists were first created for broadband deep UV imaging. They were then used with monochromatic KrF excimer laser light, then ArF and now F₂ for 157 nm imaging.¹ As a result most, if not all, photoresist companies now have plans to develop photoresist technology for 157 nm microlithography. The design of 157 nm resists, however, presents formidable challenges as most of the known photoresist materials (used at higher lithography wavelengths) absorb too strongly at these low wavelengths.

For photoresists to function properly, their films must be suitably transparent at the exposing wavelength. The introduction of progressively shorter wavelength lithographic technology has driven the development of new resist materials, as the photoresists currently used for 248 and 193 nm lithography have poor transparency at 157 nm.
The search for photoresist materials suitable for 157 nm optical lithography has a number of goals. Foremost is that the components of the resist formulation be transparent at 157 nm. For instance, the polyhydroxystyrene derivatives and polymethacrylates currently used in 248 and 193 nm lithography exhibit poor transparency at 157 nm. To this end, fluorocarbon polymers and silicon-based polymers, siloxanes and silesquioxanes, have been identified as promising new materials for 157 nm photoresists.

Theory

The ‘conventional’ UV-Vis spectral range incorporates the UV and visible portions of the electromagnetic spectrum from 190 to 900 nm. The short wavelength limit of conventional instruments is defined by the absorption of ultraviolet light having wavelengths below 190 nm by atmospheric gases. Purging such instruments with dry nitrogen will extend this limit to 175 nm. Working below this wavelength has traditionally required the use of vacuum based-techniques. By combining instrument purging with appropriate source, optics and detector, the Cary Deep UV system (DUV; Figure 1) permits measurements down to 140 nm without the need to evacuate the instrument and sample chamber.

The ‘VW’ absolute SRA (Figure 2) is designed to measure ‘mirror-like’ reflectance from a sample surface. In addition to absolute measurements, samples can be placed in both beams, allowing comparative measurements. The accessory uses a modification of the ‘VW’ configuration first described by Strong. This method calculates absolute specular reflectance by using a pair of matched mirrors to perform the calibration and measure the sample reflectance. Whereas this method relies upon a perfectly matched pair of reference mirrors, the Cary ‘VW’ absolute SRA uses one mirror on a movable 3-pin mount for both the calibration and sample reflectance measurements. This eliminates the need for expensive, perfectly matched reference mirrors.

The Cary Deep UV System, incorporating Deep UV spectrophotometer and inert nitrogen atmosphere glovebox

Figure 2. Optical diagram of the Cary ‘VW’ Absolute Specular Reflectance Accessory

The SRA features a dual ‘VW’ configuration, with one spherical mirror, and two toroidal mirrors per beam. The movable mounting of the spherical mirrors allows them to be used for both calibration and sample measurement. Hence, the same optical components are in the light path during both calibration and measurement. When a sample is mounted, the only change in the system is due to the reflectivity of the sample, and an absolute value of the reflectance is
obtained. The dual ‘VW’ configuration also permits direct comparison measurements. A reference sample may be placed in the rear position and an unknown sample in the front position. In this manner, the sample can also be directly compared to the reference.

Materials and methods
(For part numbers please see Reference 8)

Equipment:
- Cary Deep UV Spectrophotometer
- ‘VW’ Absolute Specular Reflectance Accessory
- Cary 400/500 Rear Beam Attenuator
- Cary 400/500 Extended Sample Compartment
- Nitrogen purged glovebox (Innovative Technology, Massachusetts USA)

Protocol
The ‘VW’ SRA was installed into the Cary Deep UV and aligned. Reflectance spectra were collected between 150 nm and 250 nm with the Cary Scan software, using a spectral bandwidth of 3 nm and a scan rate of 600 nm/min (Figure 3). Reduced slit height and rear beam attenuation (1.50 absorbance) were also used.

Figure 3. Instrumental settings for photoresist measurement

Replicate absolute reflectance spectra of the wafer photoresist coating were acquired as follows. Firstly, to confirm the reproducibility of the measurement technique, five scans of the coating were acquired without moving the sample. Secondly, to investigate the homogeneity of the coating, scans were acquired at five different locations on the sample surface. In each case, the sample was positioned using the sample clip supplied with the ‘VW’ accessory. The ‘Zero SRA’ baseline correction was performed prior to the acquisition of sample spectra in order to set 0 and 100 %T values. This is particularly important when measuring samples with low reflectance. With zero SRA baseline correction selected, the Cary software will automatically perform zero and 100 %T baseline corrections.

Results and discussion
The absolute specular reflectance spectra acquired can be seen in Figure 4. The five replicates acquired without moving the sample (Figure 4a) show excellent reproducibility, and demonstrate the efficacy of the measurement technique. The spectra of the photoresist obtained at five different locations on the wafer (Figure 4b) are essentially identical. This is suggestive of a uniform coating thickness and, in turn, photoresist coating homogeneity. Unfortunately, the thickness of the photoresist coating was not known, so absolute conclusions about the suitability of this resist for use at 157 nm cannot be made.

Figure 4. Replicate absolute specular reflectance scans of the photoresist coated silicon wafer; (a) without moving the sample; and, (b) at five different sampling locations
Conclusion

Using a Cary Deep UV spectrophotometer, ‘VW’ specular reflectance accessory, and nitrogen-purged glovebox, the reflectance properties of a next-generation photoresist material were investigated. The sample was characterized over the wavelength range 150 to 250 nm, with the results suggestive of a uniform photoresist coating and general coating homogeneity.

References


6. Cary UV At Work No. 082


8. Part Numbers:

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