Ultrasonic monitoring of photoresist processing

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ABSTRACT

A high frequency ultrasonic technique has been developed to monitor photoresist processing *in situ* during semiconductor manufacturing. Photoresist pre-exposure bake and development have been monitored using the sensor, and the post-exposure bake has been studied as well. The *in situ* glass transition temperature (T_g) was determined during the prebake for I-line films down to 0.6μm as well as for chemically-amplified DUV resists of similar thicknesses. Using classical reflection theory, photoresist properties such as the density, thickness, and acoustic velocity were determined during processing. This *in situ* parameter inversion method can be used to determine process endpoint if the optimal density, velocity, and thickness are predetermined. The T_g for post-exposure bake of I-line resists is expected to be the T_g of the novolac resin alone, without solvent present. Measurements using the described sensor have confirmed that the resin T_g during postbake is 118°C, the value of T_g provided by Shipley. This provides a measurement of postbake as well as a confirmation that the sensor is measuring T_g accurately. The development process was also monitored using this sensor. Results prove the usefulness of this sensor for *in situ* measurement of resist thickness changes during development. This was verified for different exposure doses and for resist coated on a wafer with circuit topography.

Keywords: Photoresist, prebake, development, ultrasonic sensor, process monitoring, semiconductor manufacturing.

1. INTRODUCTION

In current I-line and deep-UV lithography, *in situ* monitoring of photoresist processing is not required to meet design objectives. However, as feature size shrinks below sub-quarter micron, it is expected that the resist materials will be more sensitive to processing conditions during pre-exposure bake, post-exposure bake, and development. After photoresist has been spin-coated to form a sub-micron film on a silicon wafer, it is necessary to prebake the freshly spun layer of resist prior to lithographic exposure. The purpose of this step is to evaporate the solvent from the film as well as to relax the resin polymer chains into an ordered array [1]. In order to accomplish this, the resist must be heated beyond its glass transition or softening temperature and held above that temperature during evaporation. The time of prebake is crucial because if the solvent is not fully evaporated, the resist contrast can be compromised. Along with this, the temperature of prebake is also important since the resist can decompose if it is heated past its decomposition temperature. In either case, the feature size and therefore the device size will not be as expected. A sensor to detect resist cure state across the wafer would be necessary to optimize the process for each new wafer.

After the prebaked resist has been exposed, there is a post-exposure bake (PEB) step designed to produce a uniform image. Heating the resist to the post-exposure bake temperature enables diffusion of the exposed photoactive compound (PAC) within the resist, smoothing the standing waves that result from interference effects. In the case of chemically-amplified resists, the post-exposure bake is especially important since the deprotection reaction and the diffusion of photoactive compound continue throughout the PEB. A measure of this diffusion and the large changes in film properties that accompany it would be useful in characterizing the bake and the effect of its parameters on the final critical dimension of the devices. Once the resist has been through the PEB, it is developed to etch the desired circuit pattern into the resist. It is crucial that all of the soluble resist be removed by developer while the insoluble resist remains to sustain the exposed pattern. Thus, prediction and control of the development rate and time to clearance are necessary for repeatable feature size and device operation.

In the field of resist processing, some research has been completed in endpoint detection of the pre-exposure bake process[2], but the technique provides thickness information only and not information on changing elastic properties. Endpoint detection of photoresist development based on optical monitoring of thickness has been effective for over a decade[1,8,9], but this measurement still requires that the development solution be transparent to the incident light. The technique described here provides information on the studied film's elastic properties and thickness and, since it is

Part of the SPIE Conference on Metrology, Inspection, and Process Control for Microlithography XIII • Santa Clara, California • March 1999
SPIE Vol. 3677 • 0277-786X/99/$10.00

based on ultrasonic technology, it does not depend on optical transparency of the measurement environment. In this paper, ultrasonic measurement and monitoring of the prebake, postbake, and development processes are addressed. Ultrasonic technology has already been applied to the more general task of monitoring semiconductor fabrication processes[3-7]. This work involved exciting Lamb waves in silicon wafers and measuring the changes in the velocity of these waves that occurred during wafer processing. Unlike this previous work, the measurement principle of the current sensor involves exciting a high frequency longitudinal wave in the wafer and monitoring changes in the reflection coefficient of the wave as it reflects from the silicon/photoresist interface. As the resist thickness, density, and acoustic velocity change during prebake, the reflection coefficient will be altered in accordance with reflection theory; this will allow *in situ* monitoring of the process. The measurement principle and technique are described first, then the application of the sensor to photoresist development and pre- and post-exposure bake process monitoring is reported.

2. MEASUREMENT PRINCIPLE

The sensor introduced here is based in principle on the measurement of the acoustic reflection coefficient for a wave incident on the interface between silicon and a thin film. This reflection coefficient is dependent upon the elastic properties of the thin film. As with optical reflection, there can be constructive and destructive interference in a thin film that will change as the film thickness and properties change. If the film thickness is of the same order as the wavelength of the incident wave, then these interference changes manifest themselves as measurable changes in the amplitude and phase of the reflection coefficient.

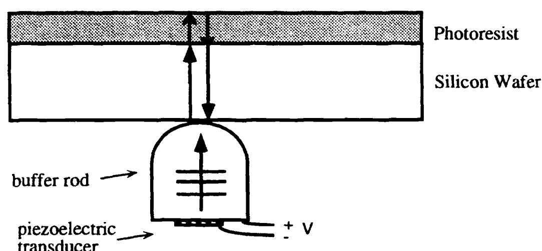

Figure 1: Illustration of sensor technology (not to scale).

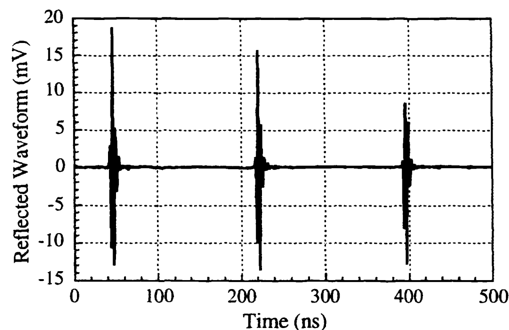

Figure 2: Sample reflected waveform used for phase calculation. The first three reflections from the silicon/photoresist interface are shown here.

Figure 1 is an illustration of the reflection measurement [10]. An 8 μm thick zinc oxide (ZnO) film is deposited on a sapphire buffer rod which is placed in contact with the back side of the wafer. The ZnO piezoelectric transducer is excited with a 20-50 V voltage spike, launching a longitudinal wave that is coupled from the buffer rod to the silicon wafer. The reflected wave can then be monitored by the same transducer; it is the change in the amplitude and phase of this reflection that will provide information regarding the resist property changes. Figure 2 shows a typical set of reflections from the silicon/resist/air interface. The reflected waveform consists of a combination of reflections from both the wafer/resist interface and the resist/air interface, however, if the resist film is about an order of magnitude less than the wavelength, then these reflections will be indistinguishable. Typical wavelengths that will be used here are 20-40 μm. The waveform phase is determined by subtracting the phases of the first two reflection signals shown at 40ns and 220ns. Subtracting the phases of the two signals allows for the removal of unrelated systematic effects such as buffer rod temperature changes. The first set of waveforms obtained is used as a reference, thus the phase change is the parameter that is measured. Data is collected at a repetition rate of 3 seconds and the phase calculated using MATLAB® software.

In order to quantify these reflections and their trends during resist processing, the reflection coefficient for a longitudinal plane wave incident on a layer separating two semi-infinite media can be calculated using classical reflection theory and is shown in Eq. 1 [11].

$$R = \left[\frac{(1 - \frac{z_1}{r_3}) \cos k_2 L + j \frac{z_2}{z_3} \sin k_2 L}{(1 + \frac{z_1}{z_3}) \cos k_2 L + j \frac{z_2}{z_3} \sin k_2 L} \right] \quad (1)$$

where k_i is the wave number and z_i is the acoustic impedance defined as:

$$k_i = \frac{2\pi f}{c_i}, \qquad z_i = \rho_i c_i$$

where the subscripts $i = 1,2,3$ represent the media of silicon, photoresist, and air, and c_i denotes the velocity of longitudinal waves in the medium and ρ_i is the density. The photoresist thickness is represented by L and frequency is given by f. We also expect a phase change in the reflected signal as the wafer changes temperature. Equation 2 governs the change in phase resulting from this wafer temperature change[12].

$$\Delta\varphi(T) = 2\pi f d \left[\frac{1}{v(T_0)(1 - k_v(T - T_0))} - \frac{1}{v(T_0)} \right] \quad (2)$$

Here, d is the silicon wafer thickness, f is the frequency of the ultrasonic signal, $v(T)$ is the velocity of a longitudinal wave in silicon at temperature T, T_0 is room temperature (25°C), and k_v is the temperature sensitivity coefficient of the wave velocity in silicon. For a given process, we expect a phase change as the acoustic impedance and thickness of the resist change. If, along with these impedance and thickness changes, there is a temperature change during the process, an additional phase change corresponding to Eq. 2 will be measured. This temperature effect can be characterized and removed from the data, leaving a measure of density, acoustic velocity, and thickness changes that can be analyzed to determine at what state the process is and whether or not it has reached completion. This measure is the phase of the reflection coefficient, plotted vs. frequency in Fig. 3 for a typical reflection measurement. Curve fitting of the theory to this plot inverts the resist characteristics at each point in the process.

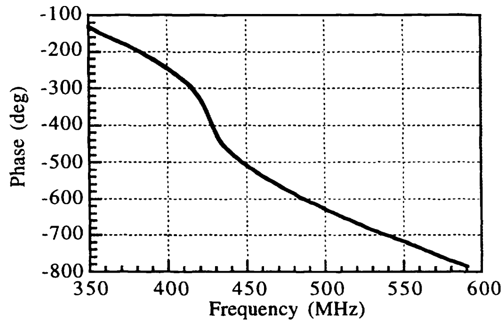

Figure 3: Typical experimental reflection phase vs. frequency curve that is used for curve fitting.

In order to invert the resist parameters of density, velocity, and thickness from the data, either one of the parameters must be known or Eq. 1 has to be rewritten in terms of only two variables. If this is not done, a unique solution will not be possible. The reflection coefficient at the silicon wafer/photoresist interface can be written in terms of two main parameters, the resist time of flight and the resist acoustic impedance. The acoustic impedance equals the density times the velocity of sound in the resist, and the time of flight is equal to the thickness of the film divided by the velocity of sound in the resist. Knowing the phase of the reflection coefficient in Fig. 3, the time of flight and resist impedance can be determined.

Knowing one of the three properties that these parameters depend upon, the other two can be determined. For example, if the thickness of the resist is known throughout the prebake, then the corresponding density and velocity changes can be determined. These properties can be correlated to the state of the prebake and the process can be stopped based on their reaching a given threshold level.

3. EXPERIMENTAL RESULTS

3.1 DEVELOPMENT MONITORING

To demonstrate the use of this transducer as a development process sensor, the phase change of the reflection coefficient was monitored during resist removal. This phase data was then inverted to find the thickness change during development. A sample trace of resist thickness vs. time during development is shown in Fig. 4. Endpoint was seen to occur in about 75 seconds, with an average development rate of about 0.1 μm/sec. The removal of this 1.5 μm thickness resulted in a phase change of 18° at 283 MHz, which agrees well with the expected phase change at this frequency. A simple calibration was completed to remove the effects of developer addition on the reflection phase. This was done for puddle development here but could be applied to either spray or immersion development too. Two other locations were also developed on the same wafer with similar results. Note that the development rate decreases as the depth into the resist increases. This variation is expected as a result of absorption of the exposure energy as it travels through the resist.

To measure the difference in development rate that results from different exposure levels, resist thickness changes were monitored during development of four samples [13]. The results are shown in Fig. 5, where the thicknesses vs. development time are plotted for 4 different exposure doses. As the exposure dose was increased from 20 to 68 mJ/cm^2, the dissolution rate initially increased sharply but then leveled off above at a dose of around 55 mJ/cm^2. One consideration in designing a sensor to monitor development or any other wafer processing step is whether or not topography on the wafer will interfere with the measurement. In a previous paper [13], this issue was addressed and it was shown that the sensor could monitor development on multi-layered 3-dimensional PMOS devices with topographical dimenstions on the order of the thickness of the resist film (0.1-1.0 μm). Another consideration was the sensitivity of the measurement to development of a resist pattern instead of the blanket film removal studied above. Calculations indicated that if a pattern of lines was developed, the change in phase would be measurable if the total area of the lines removed was greater than 1/20 the original area of resist coating.

This sensor is capable of monitoring the thickness of photoresist during lithographic development, differentiating between development rates, and monitoring development of photoresist deposited over layered topography. This technique can be applied to *in situ* monitoring of lithographic photoresist development in a manufacturing setting.

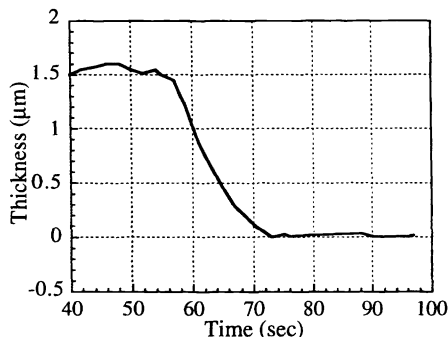

Figure 4: Inverted Resist Thickness during Development.

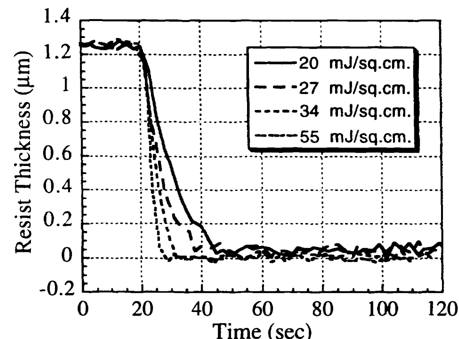

Figure 5: Average Development Rate vs. Exposure Dose.

3.2 PRE-EXPOSURE BAKE MONITORING

In a previous paper, the phase measurement technique was shown to be able to measure the glass transition temperature of solvent/resist resin mixtures during pre-exposure bake[10]. This was accomplished for Shipley 1800 series resists greater than 1 μm thick. The goal of current work was to extend this technique to resist films down to 0.4 μm in thickness as well as chemically-amplified resist films. Once this was accomplished, the parameter inversion technique described above was applied to determine the resist properties as a function of prebake.

To predict the frequency necessary to monitor the prebake of other resist thicknesses, Fig. 6 is a plot of the calculated phase transition frequency (or frequency of film resonance) vs. resist thickness. An example of the phase transition frequency is seen in Fig. 3, defined as the point at which the inflection in phase occurs. Notice in Fig. 6 that there is a sharp increase in the frequency of highest sensitivity as the films are spun thinner; it is reasonable to allow for 1-2 GHz frequency requirements since acoustic microscopy transducers have been designed beyond this range. In order to predict the transducer frequency which will provide the highest sensitivity to a given thickness measurement, it is necessary to find the frequency of the phase transition for that film thickness. To verify the solid line curve in Fig. 6 experimentally, measurements of prebake at final film thicknesses of 2.2 to 0.6 μm were conducted and the phase transition frequency determined. Shipley 1813, 1811, and 1805 resists were applied for this purpose, with the 1813 resist being the most viscous and 1805 the least. The less viscous the material, the lower the spun film thickness will be. The dashed line shows the results of this study, matching well with expected results. Results of a prebake study on a 0.6 μm film of Shipley 1805 resist are shown in Fig. 7.

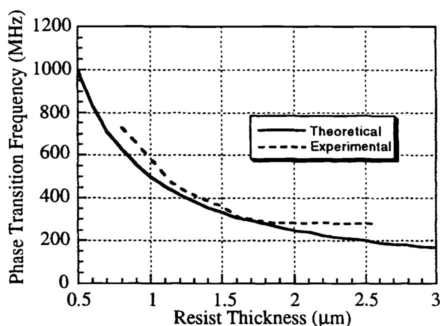

Figure 6: Theoretical and Experimental Phase Transition Frequency vs. Resist Film Thickness.

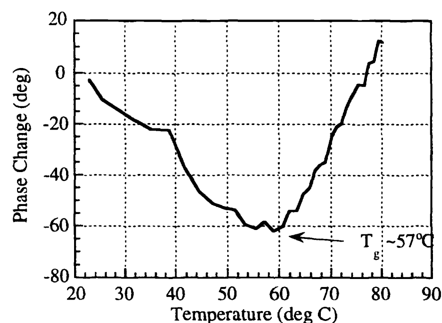

Figure 7: Phase Change vs. Temperature during Prebake, 0.6μm Shipley 1805 film, 750 MHz.

The DUV prebake experiments were conducted on Shipley APEX-E 2048 photoresist. The temperature coefficient determined in the previous section was used to subtract the temperature effects from the measured phases during prebake. The resist was spun on the wafers at 3500 rpm for 40 seconds. Results of two studies on 0.8 μm films are shown in Fig. 8 with phase change plotted versus wafer temperature during prebake. The plots indicate that the glass transition temperature occurs at about 67 and 70°C in the separate experiments. These measured prebake glass transition temperatures are higher than those measured for I-line resist films. In order to confirm the claim that the minimum in phase corresponds to the glass transition temperature, a postbake glass transition temperature measurement was completed. Once postbaked, the novolac resin of the Shipley 1800 series resists is expected to have its glass transition at 118°C. As shown in Fig. 9, this result was confirmed with the phase minimum occurring at 118°C. In some photoresist postbake processes, it is important not to exceed this temperature since the features will lose sharpness as they become fluid; in others, the goal is to exceed T_g in order to minimize contaminant diffusion. This measurement can be used as a monitoring technique for post-exposure bake of materials whose T_g is unknown; the process would be stopped once the phase curve began to flatten towards the minimum.

Next, the time of flight and impedance parameters were determined by curve fitting of the phase vs. frequency curves during prebake. A typical set of phase vs. frequency curves that are measured during resist prebake are shown in Fig. 10. The plot shows that the phase initially decreases as prebake begins (from the top solid line to the lowest solid line) and then increases after reaching a minimum (lowest dashed line to uppermost dashed line). The minimum was determined to be the glass transition temperature of the resist/solvent mixture, but the minimum was only measured at one frequency [10]. In this case, the phase was calculated over a range of frequencies instead of at one frequency.

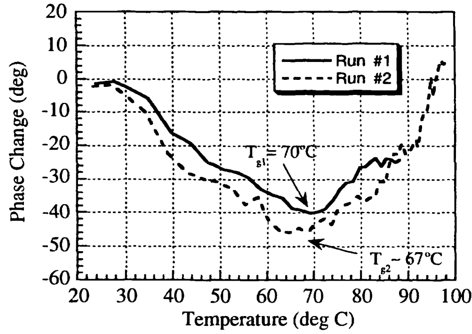

Figure 8: Phase Change vs. Temperature during Two Prebake Experiments, 0.8µm Shipley APEX-E films, 750 MHz.

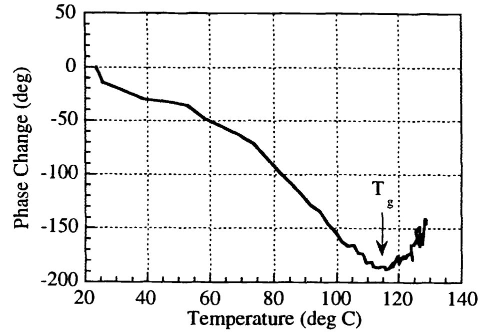

Figure 9: Determination of Postbake T_g, phase change is plotted vs. postbake temperature.

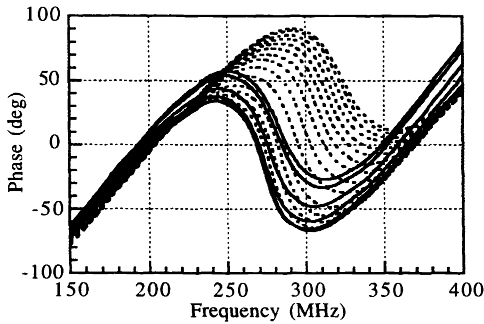

Figure 10: Sample phase vs. frequency curves measured during prebake.

Results of the parameter inversion show that the time of flight and acoustic losses reach a maximum at the glass transition temperature. This indicates that, as expected, the resist softens to the greatest extent at this temperature, causing the velocity of the resist to decrease and the thickness to increase slightly due to volume expansion. Figure 11 illustrates the time of flight inversion results for a 2 µm film of Shipley 1813 resist. The time of flight plotted vs. prebake temperature. The time of flight maximum is shown to occur at about 48°C in this figure, corresponding to the phase minimum measured by the sensor. This confirms that the resist is acoustically slowest at the glass transition temperature. Figure 12 shows that the resist impedance is also lowest around this temperature; here inverted resist impedance is plotted versus prebake temperature.

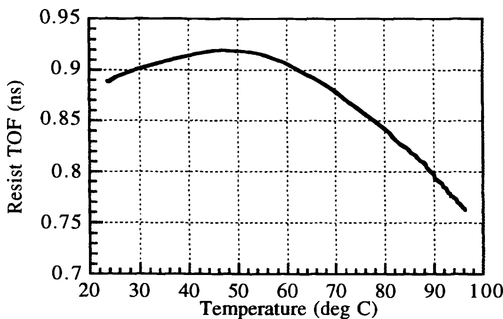

Figure 11: Time of flight inversion results, TOF plotted vs. prebake temperature.

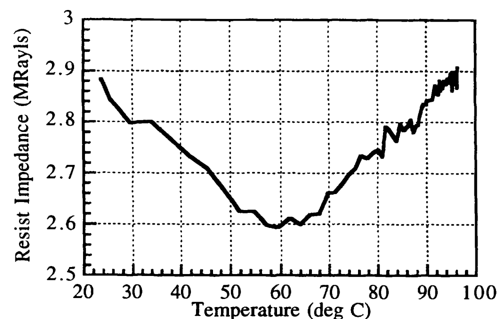

Figure 12: Resist impedance inversion results, impedance plotted vs. prebake temperature.

Another important result of the inversions was obtained by tracking the resist attenuation during prebake. The amplitude ratio of the second to the first reflection was calculated at the resonant frequency of the film with the trend in amplitude ratio changes during prebake plotted in Fig. 13. The frequency at which the amplitude is a minimum decreases

as the glass transition temperature is reached, and then increases as the solvent evaporates; this indicates a change in the resonant frequency of the film as it is processed. As can be seen from Fig. 14, a plot of the amplitude ratio vs. temperature, the amplitude ratio reaches a minimum at T_g, indicating a maximum in resist losses at that point, and then increases as the resist solidifies. So, from the time of flight and impedance inversions of the phase data, we can conclude that at the glass transition temperature, the resist acoustic velocity is a minimum and the density and velocity are also lower. From the amplitude data, it is concluded that the resist attenuation losses are a maximum at T_g. Similar results were obtained for modeling of the APEX-E resist. The next step in this research is to correlate inverted resist parameters with pre-exposure bake times and optimum critical dimension measurements.

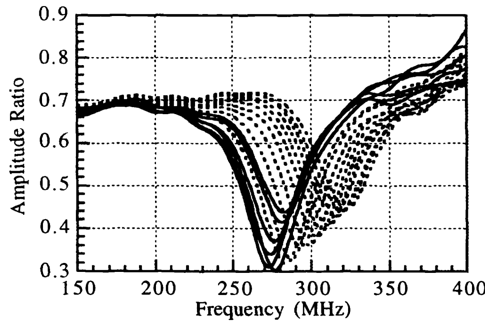

Figure 13: Amplitude trends during photoresist prebake, Shipley 1813 resist, 1.6 µm

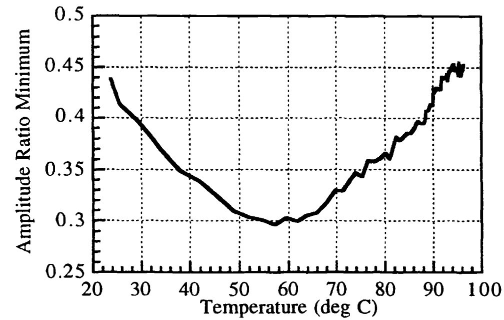

Figure 14: Amplitude ratio vs. temperature during photoresist prebake, Shipley 1813 resist 1.6 µm.

4. CONCLUSIONS

A previously-reported ultrasonic measurement of glass transition temperature was extended to include monitoring of chemically-amplified Shipley APEX-E resist and Shipley 1800 series resists spun to around 0.6 µm thick. It has also been shown to be applicable to monitoring resist development, providing thickness versus development time and development rate information for different exposure doses. An *in situ* curve fitting method was also applied to photoresist process monitoring. It was shown to provide thickness change information during photoresist development and time of flight, acoustic impedance, and attenuation data during photoresist pre-exposure bake of both I-line and chemically-amplified deep-uv range resists.

ACKNOWLEDGEMENTS

This research was funded by the Defense Advanced Research Projects Agency of the Department of Defense and monitored by the Air Force Office of Scientific Research under Grant No. F49620-95-1-0525.

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