Characterization of an Ultra High Aspect Ratio Electron Beam Resist for Nano-Lithography

S. Lewis*, D. Jeanmaire*, V. Haynes*, P. McGovern** and L. Piccirillo*

*School of Physics and Astronomy, Radio Astronomy Technology Group, The University of Manchester, Alan Turing Building, Oxford Rd, Manchester, M13 9PL, UK. Tel: +44 (0)1613062497,

Scott.Lewis@manchester.ac.uk

**NanoResists Ltd, Unit 9, Worsley Mill, Castlefield, Manchester, M15 4LG, Peter.McGovern@nanoresists.com

ABSTRACT

An electron beam resist called SML-2000 has been investigated. It has produced nano-structures with a high aspect ratio of 10:1 using an acceleration voltage of 25KV. This is significant, as comparing this result with PMMA, it was found from the Monte Carlo simulations that PMMA had inherent problems of generating secondary electrons which contribute to the proximity effect. It was clear that the SML-2000 did not suffer with these problems as 200nm structures remained after the development process.

Keywords: SML-2000, PMMA, high aspect ratio, electron beam resist, electron beam lithography, Monte Carlo Simulations.

1 INTRODUCTION

Poly(methylmethacrylate) (PMMA) is an organic electron beam resist well known to the scientific and industrial communities: it can produce features tens of nanometers in size [1]. To achieve such geometries, the resist film thickness must be around 40nm and hence, it has an aspect ratio limit of approximately 4:1 [2]. Due to the geometry of the polymer nanostructures, dry etching techniques such as inductively coupled plasma (ICP) and reactive ion etching (RIE) are preferable to transfer these nanoscaled structures to a substrate such as Silicon (Si) or Gallium Arsenide (GaAs). However, the etch rate of the semiconductor is much slower than the PMMA, which is problematic because the nano-scaled structures will not be etched deep into the substrate. As a result, transferring these nanoscaled structures with sub-10 nm geometries deep into the substrate cannot be achieved with standard PMMA resists. If the thickness of the PMMA film is increased to hundreds of nanometers, then the resultant nano-scaled structures can be driven deeper into the substrate. However, as the incident electrons penetrate through the resist, they are scattered either elastically or inelastically in arbitrary directions away from the primary beam. As a result, when the electrons clear the resist at this thickness, they may have been scattered tens to hundreds of nanometers away from the primary beam. This leads to large proximity effects, which cause the nanoscaled structures to collapse upon

development. Therefore, fabricating nano-structures with aspect ratios greater than 4:1 at this thickness cannot be achieved.

In this work a new electron beam resist called SML-2000 has been investigated to obtain a high aspect ratio to etch the nano-structures even deeper into the substrate. The results found are directly compared to traditional PMMA with the same thickness using a Monte Carlo model and experimental to determine the effects of the resist thickness.

2 EXPERIMENTAL

2.1 The Monte Carlo Simulation

The resist modeled here was PMMA with a thickness of $2\mu m$. In the model, the physical properties of the resist were that the PMMA had a density of 1.19 g/cm³ and the atomic weight of 950 000 g/mol [3]. The PMMA resist film with respective clearing dose of $1025\mu C/cm^2$ and was found from the results to be described in section 3, which shows the effects of the resist thickness.

The Monte Carlo simulation presented here is based on the model developed by Joy [4]. Electrons are incident on a PMMA film and are scattered elastically and inelastically with the PMMA molecule throughout the resist. These two scattering events are governed by two different sets of equations. Elastic scattering is determined by the screened Rutherford cross section,

$$\sigma_{elastic} = \frac{Z^2}{E^2} \frac{4\pi}{\alpha + \alpha} \left(\frac{E + 511}{E + 1024} \right)^2 cm^2 / atom, \qquad (1)$$

where E is the electron energy in keV, Z is the atomic number of the material and α is the screening factor, this compensates for the fact that the electron does not 'see' the all of the atom's charge as it is surrounded by a cloud of electrons. The mean free path is calculated from the scattering cross section is given by

$$\lambda_{elastic} = \frac{A}{N_a \rho \sigma_{elastic}}, \qquad (2)$$

where A is the atomic weight of the material and Na is Avogadro's number.

Inelastic scattering however, must use a separate relationship as there is a high probability that a secondary

electron (SE) is produced from this scattering event. Therefore, the scattering cross section is calculated using,

$$\frac{d\sigma_{inelastic}}{d\Omega} = \frac{\pi e^4}{E^2} \left(\frac{1}{\Omega^2 + 1 - \Omega^2} \right),\tag{3}$$

where ΩE is the energy of the secondary electron produced. The inelastic scattering event causes the primary electron to be deflected by an angle α given by

$$\sin^2 \alpha = \frac{2\Omega}{2 + t - t\Omega},\tag{4}$$

where t is the kinetic energy of the electron (in units of its rest mass). However the secondary electron created exits the collision at an angle γ given by,

$$\sin^2 \gamma = \frac{2 \ 1 - \Omega}{2 + t\Omega} \,, \tag{5}$$

Once the inelastic scattering cross section is calculated, the mean free path of the electron must be calculated using,

$$\lambda_{inelastic} = \frac{A}{N_a Z \rho \sigma_{inelastic}}, \tag{6}$$

The total mean free path of the electron in PMMA is the sum of the elastic and inelastic mean free paths

$$\frac{1}{\lambda_{total}} = \frac{1}{\lambda_{elastic}} + \frac{1}{\lambda_{inelastic}}.$$
 (7)

From the value of the mean free path, the statistical distance the electron will travel before it collides again can be calculated. This is achieved using the step size equation given by,

$$s = -\lambda \ln RND$$
, (8)

where λ is the total mean free path and RND is a random number between 0 and 1. This gives a distribution of step sizes with an average step size of λ .

The final step of the Monte Carlo simulation is to calculate the energy lost by the electron during the scattering event. This was done using the modified Bethe equation for the stopping power of a material and is given by,

$$\frac{dE}{dS} = 78500 \frac{Z}{AE} \ln \left(\frac{1.166 \ E + 0.85J}{J} \right),\tag{9}$$

where *J* is the mean ionization potential of the material, which was 74eV for PMMA respectively [3]. Every time the electron scatters, this energy loss value is calculated and subtracted from the current energy of the electron. Once the electron's energy falls below 0.5KeV, the electron was no longer tracked as the distance it travels in the material is very small.

2.2 Characterization of the SML-2000 resist

In this investigation PMMA and SML-2000 electron beam resist were directly compared, but first a PMMA film must be fabricated in equal thickness to that of SML-2000. This was achieved by dissolving 550 mg of PMMA with a molecular weight of 950K (obtained from Sigma – Aldrich) in the 4.45 g of Anisole (obtained from Sigma – Aldrich

97%). To ensure that the thickness of the film was approximately 2µm (when spun at 4000rpm), the ratio of PMMA to Anisole was kept at 11%. The Anisole was filtered under vacuum through a 25nm cellulose nitride membrane filter (obtained from Millipore) and the PMMA was used 'as is'. For Anisole to dissolve the PMMA, the PMMA/Anisole samples were shaken using IKA rotary/gyrative shaker for 96 h. This process produced a suitable PMMA electron beam resist.

The PMMA and SML-2000 (obtained from NanoResists) resists was spun onto 10mm×10mm silicon substrates with a spin cycle of 4000rpm for 45 seconds, followed by a softbake at 180°C for 3 minutes, both resists obtained thickness of 2µm. Both resists was then exposed using a tungsten filament in a converted Cambridge Instrument S360 Scanning Electron Microscope (SEM), which was driven by an Elphy Quantum pattern generator. The exposed pattern consisted of twenty 200nm wide lines having a length of 50µm and a period of 2.2µm. In order to view the aspect ratio, a 50 x 20µm box was exposed adjacent to the 200nm lines. This pattern was written using an acceleration voltage of 25kV, a probe current of 30pA and a dose of 1025μC/cm². The resist was developed using a solution of MIBK (Methyl IsoButyl Ketone) and IPA (IsoProPanol), in the ratio of 1:3, for 30s followed by a 40s rinse in IPA.

3 RESULTS AND ANALYSIS

From the scattering trajectories seen in figure 1, it shows that the incident electrons experience a number of collisions with the atoms in the PMMA molecule in its flight, as this process occurs; the electrons diverge away from the incident beam. Hence, as the incident electron travels through the 2µm thick PMMA resist then the number of collisions increases and therefore dramatically increases the proximity effect. This can be seen from the red lines in figure 1.

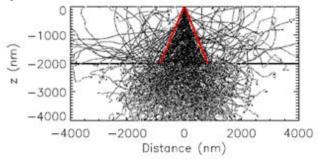


Figure 1: Forward electron scattering inside the resist film.

Exposed conventional PMMA at 25KeV.

It can be seen from the grey characteristic of figure 2 that the number of backscattered (BS) electrons produced is zero when the primary electron (PE) had an associated energy of 10 KV. This is due to the fact that none of the PE arrive at the bottom of the $2 \mu \text{m}$ thick PMMA, therefore, a clearing dose cannot be achieved. This is because the PE

does not have enough energy to travel the entire distance of the PMMA.

When more than 10% of the PE's are backscattered, these BS electrons have a large contribution to the proximity effect by the process of undercutting as the BS electrons may have enough energy to break chain in the PMMA molecule. As the associated energy of PE increases past 55KV, the number of BS electrons is approximately zero, because the associated energy of the PE is so great that it travels far into the Silicon substrate and therefore deposits all of its energy in the Silicon substrate as it comes to rest. Hence, their contribution to the proximity effect will be zero and therefore, 200nm structures can be fabricated.

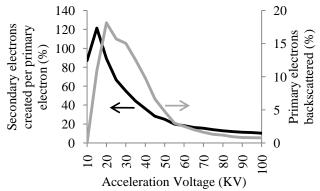


Figure 2: Number of secondary electrons created per primary electron inside the 2µm thick PMMA film, Number of electrons that are backscattered into the 2µm thick PMMA film.

It was observed from the black characteristic of figure 2 that the generation of SE appears at low acceleration voltages as the PE does not have enough energy to overcome the thickness of the PMMA ($2\mu m$). When a SE is generated, it exits the collision at a very large angle following Equ. 4. For example, a SE generated with an energy of 500eV will exit the collision with an angle of 80°. This is why the SE plays a major role in producing the 'proximity effect'. For this material the generation of most of SE occurs between 15 and 25KV and therefore is the worst accelerating voltages to use when fabricating 200nm structures or below as the SE will contribute to a large portion to the proximity effect. However, above 50KV, the generation of SE does not occur

because the energy associated to the PE is large and hence inelastic scattering rarely occurs. Therefore, to produce 200nm structures or below in 2µm thick PMMA can only be achieved using high accelerating voltages above 50KV. Figure 3 shows the resultant nano structures after the development stage. These structures seen here were exposed directly written into PMMA with a thickness of 2um. In the micrograph the spaces have been exposed to the

It is clear that the nano structures have collapsed. After development, the resultant thickness of the structures had decreased by half to 1 µm. It can be seen from figure 3 that

electron beam.

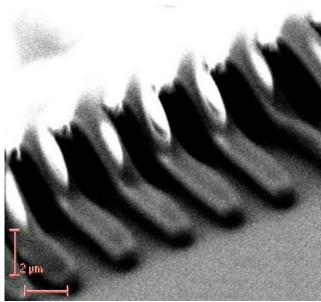


Figure 3: SEM image of 450nm features written in 2µm thick PMMA viewed at an angle of 75°.

the area of the exposure had increased from 200 to 450nm. The SE had increased the overall size of the space.

Figure 2 confirms this effect as at an acceleration voltage of 25KV, approximately 70% of PE produces a SE as they scatter. Therefore, this large number of SE will have a large impact on the proximity effects, hence, increasing the write volume.

Looking closer at figure 2, 15.5% of PE are backscattered and contribute to the proximity effects by the undercutting process discussed earlier, thus the PMMA resist thickness had decreased. The conclusion is that with these feature sizes, the aspect ratio of 4.4:1 cannot be achieved.

The SEM images of figure 4, shows a side and a high magnification view of the 2.2 μ m period grating. The exposed spaces were measured to be 200nm wide. Therefore, as the resist thickness was 2 μ m this gives an aspect ratio of 10:1.

For the SML-2000 resist to produce these nano-structures, it is evident that the inelastic scattering and backscattered electron processes do not occur as frequent as it does at 25KV in conventional PMMA; that is seen in figure 3. This is due to the nature of the molecular properties of the SML-2000 resist. Figure 4 demonstrates that smaller feature sizes can be achieved by the SML-2000 resist by confining the forward scattering electrons to the incident beam inside the resist. However, a high exposure dose is required to clear the thickness of the resist. But it is apparent that the SE does not occur as the exposure of 200nm lines have not been increased as seen in figure 5. Therefore, the proximity effects appear to be negligible.

This is a significant result as the resist thickness is approximately 2.5 times larger than standard PMMA, when fabricating 200nm features, hence, these nano-structures will be etched 2.5 times deeper into the substrate.

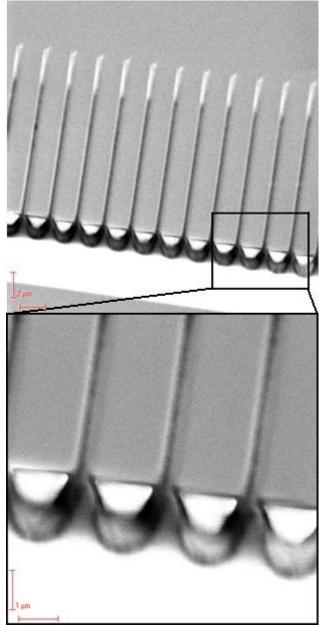


Figure 4: SEM image of 200nm features written in SML-2000 viewed at an angle of 75°.

In addition to this, a considerable increase of metal can be deposited (via the evaporation process) on to the Silicon substrate and therefore, lifted off without the use of a second copolymer. Hence, this lowers the overall cost of lithography processing step.

4 CONCLUSIONS

An electron beam resist called SML-2000 has been investigated to produce a high aspect ratio. The aspect ratio that was obtained was 10:1. It was found that this was 2.5 times larger than that of PMMA.

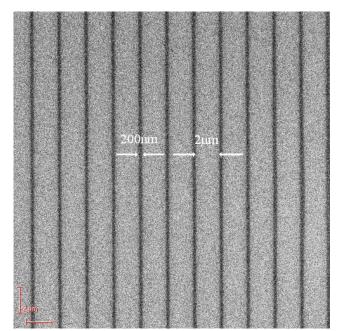


Figure 5: A top view of the 2µm structures and 200nm spaces.

When comparing this result with PMMA it was found that the Monte Carlo simulations showed that PMMA had inherent problems which consisted of secondary electrons generated that diverge away from primary electron beam giving rise to a wider trench. Also the simulation demonstrated that 15.5% were backscattered electrons which had an impact on the resultant developed feature by the undercutting process.

It was clear that the SML-2000 did not suffer with these problems as the 200nm structures remained after the development process. Hence, the proximity effect was negligible.

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