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Large contrast enhancement by sonication assisted cold development process for low dose and ultrahigh resolution patterning on ZEP520A positive tone resist

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The authors demonstrate a robust, low dose, high contrast, and ultrahigh resolution patterning process based on sonication assisted development of ZEP520A positive tone resist in both room and cold temperature. The contrast as high as $\gamma \sim 25$ and $\gamma \sim 9.14$ can readily be achieved in 6 °C and room temperature development, respectively, in diluted n-amyl acetate solution. The high contrast is demonstrated on 90 nm thick ZEP resist at 20 kV acceleration voltage, from which 20 nm thick titanium lift-off of 60 nm pitch lines and 50 nm pitch dots can be successfully achieved. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.4739053]

I. INTRODUCTION

Ultradense and high throughput nanofabrication is the motivation for the cost-effective and ultrahigh resolution patterning based on electron beam lithography (EBL). The two key factors for achieving high resolution are the beam spot size and the proximity effects, which depend on resist chemistry, resist thickness, and development processes. Patterning of sub-30 nm structures has been demonstrated using EBL based on different resists, most of which is based on high electron energy (50–100 keV).¹ Most of the resolution enhancement approaches were demonstrated in commonly used positive tone resists, such as the poly(methylmethacrylate) (PMMA) and ZEP520, for example by using nonstandard developer^{2–5} and cold development.^{6–12}

Sub-10 nm feature width at 40 nm pitch has been demonstrated in PMMA resist using isopropyl alcohol (IPA) as the nonstandard developer² at very high electron-beam (e-beam) dose of $\sim 5000 \mu\text{C}/\text{cm}^2$ and 30 keV energy on 40 nm resist thickness. The same approach is also adopted for ZEP520 resist,⁵ in which sub-25 nm pitch was achieved on 50 nm thick resist at 100 kV at the required dose of 20–50 mC/cm². Ultrahigh resolution patterning therefore can be achieved using very weak developer, but at the expense of very large e-beam dose.

Cold development, on the other hand, seems to show more promise not only for being a cost-effective approach, but also for reducing line edge roughness.^{6,10} The reason for such resolution enhancement is because the dissolution rate of the exposed resist decreases at lower temperature. This, in turn, gives steeper resist contrast curve, which plots the remaining resist thickness as a function of logarithmic e-beam dose. Intuitively, higher contrast (γ) is to be expected at lower temperature. The effect of cold development has been explored in both PMMA (Refs. 7–9) and ZEP520A resist^{6,10–12} with the achievable resist contrasts of $\gamma \sim 14$ (for PMMA)⁷ and $\gamma \sim 8$ (for ZEP520A).¹⁰

Although ultrahigh resolution patterns with 30–60 nm pitch have been demonstrated on both resists, the patterns are typically fabricated on a thin resist (<50 nm), at very low temperature (<−10 °C), at high voltage (≥ 30 kV), and requiring rather large e-beam dose ($>200 \mu\text{C}/\text{cm}^2$). Meanwhile, the resist thickness sets the limit to the maximum deposited metal thickness (for lift-off process) and etch-depth (for dry etch process) during pattern transfer stage. Therefore, a more robust process is necessary by which ultrahigh resolution patterns can be realized in thicker resist at moderately low temperature and low e-beam clearing dose.

In this paper, the resolution enhancement based on incorporation of slight sonication during cold development will be investigated for ZEP520A resist. Although the role of sonication has been previously studied in PMMA resist,^{9,13} its effect in ZEP520A, to the best of our knowledge, has not yet been explored. Based on sonication assisted development at 6 °C, a very high contrast of $\gamma \sim 25$ will be demonstrated. In addition, based on 90 nm thick resist and 20 kV acceleration voltage, 60 nm pitch lines and 50 nm pitch dots of 20 nm Ti thickness are realized at less than $200 \mu\text{C}/\text{cm}^2$ e-beam dose.

II. EXPERIMENTAL SETUP

The positive tone resist used in this work is ZEP520A from Nippon Zeon. The diluted ZEP520 resist (in 1:1 ratio) was spin coated at 4000 rpm for 60 s and prebaked at 180 °C for 2 min, giving by default resist thickness of 90 nm on $5 \times 5 \text{ mm}^2$ silicon sample. The samples were exposed by Raith e_LiNE electron beam lithography tool at 20 kV acceleration voltage with 7.5 and 10 μm aperture sizes, corresponding to beam current of 22 and 43 pA, respectively. The acceleration voltage of 20 kV was used in order to have a reasonably small undercut and e-beam clearing dose, and also to have a reasonable amount of beam current to ensure short writing time.

The samples were developed in various solutions in different temperatures and rinsed in different solutions at room temperature. The beaker containing the developer solution was normally placed inside the refrigerator or warmed up in natural clean room ambient for more than 1 h in order to

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obtain cold temperature (i.e., 6 °C from thermometer reading) and room temperature (i.e., 22 °C) process, respectively. The contrast curves were obtained from thickness characterization (by DekTak surface profiler) of an array of $20 \times 55 \mu\text{m}^2$ boxes patterned by varying e-beam doses from 10 to $150 \mu\text{C}/\text{cm}^2$.

III. ENHANCEMENT OF CONTRAST

A. Standard development process

ZEP520A consists of the alternating α -chloromethacrylate and α -methylstyrene in its molecular structure,¹⁴ which leads to the increased sensitivity due to α -chlorine atoms, and increased dry etch resistance due to the introduction of α -phenyl group.¹⁵

In order to understand the development mechanism of ZEP resist, in the first set of experiments we characterized the contrast curves of standard development processes based on standard developer solution n-amyl acetate (i.e., ZED-N50, from Nippon Zeon), rinsed in two different solutions. The exposed samples were developed for 15 s in ZED-N50 at room temperature, followed by methylisobutylketone (MIBK) or IPA rinse for 30 s. The contrast curves corresponding to the two cases are shown in Fig. 2, where the normalized residual thickness is plotted as a function of e-beam dose. It can be seen that while the dose-to-clear of both cases only slightly differ, the difference in resist contrast is clearly observed. It is important to note that despite the same develop time in the two cases, the sensitivity for the MIBK rinsing is higher than that for the IPA rinsing.

The tail can clearly be observed at high e-beam doses for the IPA rinse case. Such a tail is well known to impose limitation on the achievable resolution.⁹ The plausible explanation on the origin of the tail is that the resist adhering to the substrate tends to have more molecular weight, which thus requires more e-beam dose to dissolve.¹⁶ MIBK is a much stronger solvent compared to IPA, and thus is able to remove the exposed resists, which have more molecular weight. This explains the absence of tail in the MIBK rinsing case. This is illustrated at $20 \mu\text{C}/\text{cm}^2$ e-beam dose, where $\sim 55\%$ of the resist is removed when MIBK is used as the rinsing agent. This is unlike the IPA rinsing case, in which the resist removal is almost negligible, indicating that polymer chain scission has already happened at a given dose but the molecular weight is still too large for the IPA to dissolve. On the other hand, for the MIBK case, the molecular weight is sufficiently small to be dissolved, which makes it rather insensitive to dose variation. The measured contrasts of both cases are $\gamma = 4.34$ (MIBK) and $\gamma = 4.54$ (IPA).

The development rate is defined as the rate at which the resist is removed during development, as calculated by dividing the removed etch thickness over the development time (t_{dev}). The development rate for processes in Fig. 1 is presented in Fig. 2. By comparing the IPA rinsing case in different resist thicknesses, i.e., (1) and (2), one can see that the development rate of (2) follows that of (1) and saturates after dose-to-clear. The 120 nm resist thickness was realized by diluting the ZEP520A in a 3:2 ratio at 4000 rpm spin speed.

FIG. 1. (Color online) Standard developments using different rinse solutions at room temperature. The normalized remaining resist thickness is deduced from the surface profiler measurement h . The initial resist thickness is measured as h_0 .

This means that development rate is proportional to the resist thickness, which is consistent with the fact that e-beam penetration is normally more than the resist thickness. By comparing (2) and (3), one can observe that the development rate of both cases initially differs but eventually converges to rather similar rates after dose-to-clear, where the slight difference in development rates is only caused by $\sim 10\text{nm}$ difference in resist thickness. This is expected since the polymer chains become sufficiently short for both rinsers to dissolve.

B. Effect of diluted developer in resist contrast

In the second set of experiments, the standard developer was diluted in IPA in 1:1 ratio with the development time by default increased to $t_{\text{dev}} = 30\text{ s}$ and the rinsing time fixed to $t_{\text{rinse}} = 60\text{ s}$. The development scenario for this set of

FIG. 2. (Color online) Actual development rate based on standard n-amyl acetate (ZED-N50) developer solution for different rinser and varying resist thicknesses. The development rate depends on the resist thickness. This is attributed to the fact that the e-beam has penetrated much deeper than the resist thickness. The development time for each process is (1) $t_{\text{dev}} = 10\text{ s}$, (2) $t_{\text{dev}} = 15\text{ s}$, and (3) $t_{\text{dev}} = 15\text{ s}$.

Fig. 3. (Color online) Different contrast curves from different developer and rinse solutions: (1) 30 s ZED-N50:IPA followed by 30 s IPA, (2) 25 s ZED-N50:IPA followed by 30 s IPA, (3) 30 s ZED-N50:IPA followed by 30 s MIBK:3IPA, and (4) 30 s ZED-N50:IPA followed by 15 s MIBK. Different tail in each contrast curve shows the important role of the rinse solution.

experiments is still at room temperature. Figure 3 shows the contrast curves corresponding to new developer in different rinsing solutions. The rinse solutions have different dissolving strength, which were chosen to be IPA, MIBK:IPA = 1:3 (denoted as MIBK:3IPA for simplicity), and MIBK. The case of IPA rinse is denoted in (1), which expectedly exhibits higher dose-to-clear compared to that in Fig. 1. The contrast for (1) was measured to be $\gamma = 4.76$. In order to investigate the role of development time in the new developer, the development time is slightly decreased to 25 s. As denoted by (2) in Fig. 3, it can be seen that the contrast curve exhibits longer tail compared to that in (1). As the rinse solution was changed to MIBK:3IPA, as denoted by (3), one can see that the dose-to-clear is not much different from that in (1), except for the transitional region, which shifts to the left. The measured contrast for (3) is $\gamma = 4.54$.

In MIBK rinse, as denoted by (4), one can see that the transitional region shifts further to the left, corresponding to a contrast of $\gamma = 5.26$. It is interesting to note that the dose-to-clear of (4) in Fig. 3 only slightly differs from the MIBK rinsing in Fig. 1. This suggests that decreasing the developer strength has no influence in dose-to-clear since MIBK is indifferent to the variation of molecular weight in dissolving the exposed resist. However, the contrast increases from $\gamma = 4.34$ (standard developer) to $\gamma = 5.26$ (new developer). The above-presented comparisons indeed suggest that the rinse solution has more roles in determining the resist sensitivity, as indicated by the dose corresponding to 50% resist removal (D_{50}). It can be observed that the sensitivity progressively increases when the rinse solution is varied from IPA toward MIBK.

C. Effect of temperature and sonication in resist contrast

In the third set of experiments, the developments were done in room (22 °C) and cold temperature (6 °C), while the

rinse solution was fixed to room temperature. The developer and rinse solution was fixed to ZED-N50:IPA = 1:1 and IPA, respectively. The role of sonication during the development and rinse process was also investigated, where the sonication time was fixed to $t_{\text{sonicate}} = 10$ s for both development and rinsing stages. The development time is changed to $t_{\text{dev}} = 40$ s, while the rinsing time is fixed to $t_{\text{rinse}} = 60$ s. In order not to destroy the nanopatterns, the sonication strength is fixed to the lowest value during ultrasonic bath.

Note that the sonication was introduced within the first 30 s of development time (from $t_{\text{dev}} = 10$ s to $t_{\text{dev}} = 20$ s) for the purpose of comparison with the second set of experiments. Similarly, the sonication in rinse stage was also introduced from $t_{\text{rinse}} = 10$ s to $t_{\text{rinse}} = 20$ s. The resist thicknesses were fixed to 90 nm. From Fig. 4(a), one can see that a slight sonication during development process (circle markers) is sufficient to remove the tail that is present in the room temperature process (square markers). After sonication, the sensitivity has increased from $D_{50} = 65 \mu\text{C}/\text{cm}^2$ to $D_{50} = 50 \mu\text{C}/\text{cm}^2$. In addition, this gives a much sharper contrast of $\gamma = 9.14 \pm 0.83$ compared to that of the unsonicated room temperature process $\gamma = 4.76$ [i.e., the (1) in Fig. 3]. The standard deviation in the measured contrast in the sonicated case was obtained from the repeatable contrast measurements of different samples based on the same process.

Likewise, the case for cold development is presented in Fig. 4(b), where the circle and square markers denote the sonicated and unsonicated cases, respectively. Again, the unsonicated case exhibits a rather long tail in the high dose region (to the extent of $\sim 150 \mu\text{C}/\text{cm}^2$), which is definitely much longer compared to the room temperature case. This is consistent with the fact that ZEP520A development process is a thermal activation process which follows Arrhenius relationship,⁶ i.e., $\sim \exp(-E_a/kT)$, where E_a is the activation energy, k is the Boltzmann's constant, and T is the developer temperature. Lowering the temperature reduces the resist dissolution rate, which makes the resist increasingly difficult to remove even at high dose. Although such tail can be removed by MIBK rinse, as already demonstrated in this paper, the indiscriminate rinsing in MIBK will result in a decreased contrast.

This is where sonication can be proposed as a feasible way to enhance the dissolution rate of the exposed resist while still retaining the "soft" resist during the rinsing. As shown in Fig. 4(b), the tail for the cold development is completely removed without significantly changing the sensitivity. This is contrasted with the change of sensitivity in the room temperature case, which is consistent with the thermal activation process during development. The standard cold development case, i.e., based on cold N50 (for 15 s) development and cold MIBK rinse (for 30 s), is also presented, which has measured contrast of $\gamma \sim 8.33$. This is comparable to that in Ref. 10, which has $\gamma \sim 8$ for -20°C development in xylene. One can see that the performance of the sonicated room temperature development ($\gamma \sim 9.14$) is slightly higher than that of the standard cold development ($\gamma \sim 8.33$). However, the sensitivity for the standard cold development case

FIG. 4. (Color online) Contrast curves for the unsonicated (box) and sonicated (circle) in (a) room temperature, 22 °C and (b) cold temperature, 6 °C. (c) Measured contrast as a function of sensitivity (D_{50}) from different development conditions. The role of sonication in contrast enhancement is clearly evident. The unsonicated case for (a) and (b) are represented in (c) by hollow circle and hollow triangle markers, respectively.

($D_{50} \sim 38 \mu\text{C}/\text{cm}^2$) is still better than the sonicated room temperature case ($D_{50} \sim 50 \mu\text{C}/\text{cm}^2$).

The measured contrast for the sonicated cold development was $\gamma = 25.14 \pm 5.83$, which is more than two times higher than for the sonicated room temperature development and approximately three times higher than for standard cold development. The contrast values had been repeatedly measured for four separate samples, which were based on the same sonication time, development temperature, and the same resist thickness and exposure dose variation. The rather large uncertainty in the measured contrast originated from the difficulty of obtaining thickness measurement around the transitional area. In this work, the thickness measurement was carried out at 1 mg stylus force to prevent resist shoveling during scanning around transitional dose. The plot of measured contrasts as a function of sensitivity (D_{50}) for the whole sets of experiments is shown in Fig. 4(c), where the solid (hollow) circle and triangular markers represent the development process in Figs. 4(a) and 4(b) with (without) sonication, while the hollow rectangular markers represent the rest of the processes described in this paper.

It can be seen that the contrast is limited to $\gamma \sim 5$ for development process without sonication (see hollow rectangular markers). However, as sonication was introduced during room temperature development, one can see the contrast enhancement of approximately two times, as denoted by the solid circle marker. This is also the case for the cold development case, where a contrast enhancement of approximately five times was observed. This clearly shows that sonication is the necessary aspect to break the inherent limitation observed in hollow rectangular markers.

Another perspective is shown in Fig. 5, which plots the normalized development rates for different processes presented in this paper. Here, to avoid confusion the resist thickness was chosen to be 80–90 nm. It can be seen that the normalized development rate for the standard developer (ZED-N50), as represented by (1), is about two times faster

FIG. 5. (Color online) Normalized development rate for 80–90 nm resist thickness under different development conditions. In room temperature: (1) ZED-N50 $\rightarrow$ IPA, (2) ZED-N50:IPA $\rightarrow$ MIBK, (3) ZED-N50:IPA $\rightarrow$ MIBK:3IPA, (4) ZED-N50:IPA $\rightarrow$ IPA, (5) ZED-N50:IPA $\rightarrow$ IPA with 10 s sonication; and in cold temperature ($\sim 6^\circ\text{C}$): (6) N50:IPA $\rightarrow$ IPA with 10 s sonication. Here, the sonication is implemented from $t = 10$ s to $t = 20$ s. Since all the exposed resist is completely removed after 30 s of development process, the development rates in (5) and (6) were deduced by assuming $t_{\text{dev}} = 30$ s, instead of $t_{\text{dev}} = 40$ s.

compared to those based on new developer (ZED-N50:IPA), as represented by (2), (3), and (4). This is quite expected since the IPA does not play a crucial role in developing the exposed resist and merely reduces the developer concentration by a factor of ~ 2 . The impact of sonication is clearly seen by comparing (4) and (5) where a slight mechanical agitation dramatically enhances the development rate. The same can be observed for (6), which represents the development rate for sonicated cold temperature development (the unsonicated cold temperature case is not shown here to avoid confusion). The contrast curves of sonicated room and cold temperature development are compared to those based on standard development case in Fig. 6.

Clearly, the contrast curve has evolved from high sensitivity and moderately sloped response in Fig. 6(a) to moderate sensitivity and almost vertically sloped response in Fig. 6(d). Based on these three sets of experiments, we have demonstrated that a remarkably high contrast ($\gamma = 25.14 \pm 5.83$) can readily be achieved with moderately cool temperature (6°C) and at relatively low clearing dose ($D_{100} < 100 \mu\text{C}/\text{cm}^2$).

IV. NANOPATTERNING

The achievable resolution is not only dependent on γ , but also on electron beam profiles, such as forward/backward electron scatterings and the e-beam depth-of-focus. The former determines “vertical contrast,” while the latter determines “lateral contrast.” Here, we explore e-beam writing strategy to improve lateral contrast for high resolution patterning. The important aspects for achieving high density patterns are small e-beam divergence angle and small electron wavelength. While both of the above-mentioned aspects can be obtained in high acceleration voltage, the required dose-to-clear inevitably becomes significantly larger because the electron energy loss is inversely dependent on the electron energy.¹⁷ In addition, because of much higher e-beam dose, high acceleration voltage e-beam tends to impart more substrate damage.

FIG. 6. (Color online) Contrast curve for different development strategies: (a) N50 $\rightarrow$ MIBK (Room Temp), (b) N50 $\rightarrow$ MIBK (Cold Temp), (c) N50:IPA $\rightarrow$ IPA with sonication at Room Temp, and (d) N50:IPA $\rightarrow$ IPA with sonication at Cold Temp.

The e-beam spot cannot go arbitrarily small since it is limited by the size of the resist molecule, which is about 5–10 nm. This suggests that decreasing electron wavelength in high acceleration voltage does not always lead to increased resolution. In this work, we explore the method to mimic the characteristics of high voltage beam by adjusting divergence angle and depth-of-focus (DOF) of low-voltage e-beam. It should be noted that in the electron beam situation, the divergence angle also depends on the forward scattering events, with scattering angle inversely dependent on electron energy. This makes the “numerical aperture” in e-beam not only dependent on aperture size and working distance, but also on acceleration voltage. However, the distribution of electron scatterings causing resist bond breaking mostly follows e-beam profile within the resist because forward scattering events merely introduce additional angle into the existing e-beam characteristics. Thus, optics analogy can still be employed to derive qualitative relations between resolution, depth-of-focus, and beam divergence angle.

As illustrated in Fig. 7, the resolution in optics is determined by the acceptance angle of the light beam, as commonly characterized by numerical aperture ($\text{NA} = \sin \theta$), i.e., $p = \lambda/\text{NA}$, where p is the resolvable pitch and λ is the wavelength of light. The beam divergence angle is related by $\theta = \tan^{-1}(D/2f)$, where D and f are the aperture size and working distance, respectively. Thus, in terms of aperture size and working distance, the numerical aperture can be expressed as $\text{NA} \sim D/2f$. In the maximum resolution, the beam spot size Δx is therefore half of the resolvable pitch, i.e., $\Delta x \equiv p/2 = \lambda/(2\text{NA})$. The depth-of-focus, on the other hand, can be derived by using a trigonometric relation $\tan \theta = \Delta x/\Delta z$ (where $\tan \theta \cong \sin \theta = \text{NA}$ for a small angle), which gives $\Delta z \equiv \text{DOF} = \lambda/(2\text{NA}^2)$. It should be noted that the spot size is not only defined by Rayleigh limit, but also by spherical aberration. Although derived from the assumption that the light is monochromatic, we believe the relations still hold true for the case of polychromatic light, where chromatic aberration is present. Despite its oversimplified form, the optics analogy is sufficient to point out basic relations between resolution, beam spot size, and depth-of-focus.

Likewise for the e-beam case, both DOF and resolution primarily depend on NA, which is a function of aperture size (D) and working distance (f). The trade-off between spot

FIG. 7. (Color online) Optical analog of e-beam for a given aperture size (D), e-beam divergence angle (θ), working distance (f), depth-of-focus (DOF), and numerical aperture (NA).

size and DOF is clearly seen where an increase of DOF (or decreased beam divergence angle) is obtained at the expense of increased spot size. The relation between NA and e-beam spot size can be verified in the contamination dot burning stage for different aperture sizes. The spot size was repeatedly measured as ~ 16 nm (for $20\text{ }\mu\text{m}$ aperture size) and ~ 30 nm (for $10\text{ }\mu\text{m}$ aperture size), which clearly shows the inverse dependence of spot size on aperture size. Note that DOF is more sensitively dependent on NA than is the spot size, e.g., a decrease of NA by two times leads to a four times increase of DOF but only a two times increase of beam spot size. Since the resolution is characterized more by the pitch than by individual feature width, and that the resolution is more dependent on resist undercut and proximity effects than on individual beam spots, this seems to suggest that increasing DOF (by decreasing NA) is more important than decreasing spot size (by increasing NA).

In order to ensure large depth of focus, the patterning was carried out at working distance of ~ 9 mm with 7.5 and $10\text{ }\mu\text{m}$ aperture sizes. The beam current was measured to be 22 pA (for $7.5\text{ }\mu\text{m}$ aperture size) and 43 pA (for $10\text{ }\mu\text{m}$ aperture size). The SEM of L-shape gratings for different development processes is shown in Fig. 9, where the resist thickness is 90 nm and the L-shaped gratings were written as single pixel lines at 6 nm line step. The case of standard development process is shown in Fig. 8(a), while the case of sonicated cold development is shown in Figs. 8(b)–8(d). The aperture size for the standard and the sonicated development case is 10 and $7.5\text{ }\mu\text{m}$, respectively. The lowest pitch for the standard development process is found to be 80 nm , with the feature width of $\sim 36\text{ nm}$. On the other hand, the pitch is clearly resolvable down to 60 nm for the sonicated cold development case. The case for 50 nm pitch is presented in

Fig. 8. (Color online) SEM L-shape gratings for: (a) standard development process (pitch = 80 nm); sonicated cold development when (b) pitch = 70 nm , (c) pitch = 60 nm , and (d) pitch = 50 nm . The e-beam dose is 480 pC/cm . The length of the scale bar is 200 nm .

Fig. 9. Rectangular mesh structure for different pitches in sonication assisted cold development process.

Fig. 8(d), where 50 nm pitch lines can still be resolved but the patterns collapse due to serious undercut caused by proximity effect. This can be mitigated if the resist is thinner. The feature width for the sonicated cold development case is measured to be $\sim 23\text{ nm}$. Note that the sonication assisted development processes [in Figs. 8(b)–8(d)] were also carried out for $10\text{ }\mu\text{m}$ aperture size, where more pattern collapses are observed even at 70 nm pitch lines. This clearly shows the dependence of DOF on aperture size, as previously suggested by the optics analogy.

The proximity effect in sonicated cold development case is illustrated in the rectangular meshes shown in Fig. 9. In the nonoverlapping area, the pitch down to 60 nm is clearly demonstrated, which is consistent to those in the L-grating shown earlier. In the overlapping area, one can expect the e-beam dose to double for every intersection, which results in increased pattern collapse as the pitch is decreased from 100 down to 60 nm . Furthermore, the edge effects in overlapping areas are brighter, which is to be expected since more e-beam dose at intersecting lines gives deeper undercut profile.

For pattern transfer, lift-off process is preferable to dry etching because dry etch process does not necessarily indicate that all the exposed resist has been removed during development. Moreover, since residual resist is also etched during dry etch process, it is not possible to identify whether the pattern is underdeveloped or overdeveloped. The above-mentioned concerns can be readily addressed by lift-off process, where good undercut sidewall (corresponding to optimized e-beam dose) and total resist removal in the exposed areas are the prerequisites for a successful lift-off. The lowest achievable pitch corresponds to the situation where the feature width is the same as the half-pitch.

The lift-off of 20 nm thick Ti metals in L-shaped gratings and rectangular mesh structures are shown in Fig. 10. The deposition was carried out by e-beam evaporation (Edwards 306), with the current and deposition rate of 70 mA and

FIG. 10. Lift-off results of L-shape gratings and rectangular mesh structure for 60 and 100 nm pitches. The e-beam dose is 360 pC/cm, except for the rectangular mesh for 60 nm pitch (320 pC/cm).

0.05 nm/s, respectively. The sample was then soaked in Dimethylacetamide (ZDMAC) solution for 10 min for lift-off. The lift-off patterns closely follow the patterns in Fig. 9. The residual resist is clearly noticed at the outermost patterns. This is expected since the effective dose at the outermost pattern is relatively lower compared to those around the center (there was no proximity correction implemented in all our experiments), resulting in metal deposition at the

resist sidewall before lift-off. The average Ti metal width is ~ 23 nm.

Finally, the lift-off of 20 nm thick Ti dot arrays at 50 nm pitch is shown in Fig. 11. Each dot was written as a single pixel ring with 6 nm diameter (at 360 pC/cm), instead of as dot exposure. The repeatability of this process is illustrated in Fig. 11(a), where the 10×10 dot arrays are repeated in 3×3 array form. Figure 11(b) shows the SEM image of the individual 10×10 dot array, where the measured dot size is ~ 23 nm. The fact that the feature width is about half of the pitch suggests that 50 nm is the lowest achievable pitch based on our process (1:1 line and spacing structure).

V. CONCLUSIONS

We have demonstrated large contrast enhancement of ZEP520A resist by modification of the developer solution and introducing sonication during development process, which gives measured contrasts of $\gamma \sim 9$ (at 22 °C) and $\gamma \sim 25$ (at 6 °C) at e-beam dose smaller than $100 \mu\text{C}/\text{cm}^2$. Dense patterning is realized on 90 nm thick ZEP520A resist based on 20 kV acceleration voltage at 6 °C development process, where the 60 nm pitch and 23 nm feature width can be obtained with high repeatability. Pattern transfer is also demonstrated in 20 nm thick Ti lift-off at lowest achievable pitch of 50 nm and feature width of ~ 23 nm.

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FIG. 11. (Color online) Lift-off results of 50 nm pitch dots. The thickness of Ti metal is 20 nm, and the resist thickness is 90 nm. The SEM of (a) 3×3 arrays of 10×10 dots, and (b) 10×10 dots. The dose is 360 pC/cm.

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