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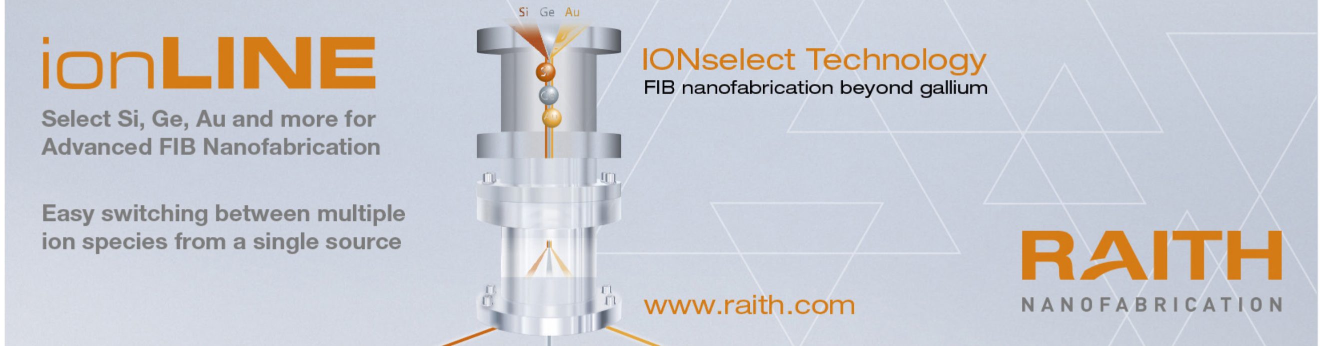

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Lift-off with solvent for negative resist using low energy electron beam exposure

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Lift-off and direct etch are the two most popular pattern transfer methods for electron beam lithography. For some applications negative resist would offer significantly less exposure time than positive one. Unfortunately, lift-off using negative resist is very challenging because the resist profile is typically positively tapered due to electron forward scattering, and upon exposure, negative resist is cross-linked and thus insoluble in solvents. Here, the authors will show that low energy exposure can circumvent both issues simultaneously, and the authors achieved liftoff of Cr with polystyrene resist using a solvent xylene. Moreover, low energy exposure offers proportionally higher resist sensitivity. Lastly, since low energy electrons are mostly stopped inside the resist layer, radiation damage to the sublayer is greatly reduced. Thus, the current method may be employed to fabricate metal nanostructures on top of an organic conducting layer. © *2014 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4901012]

I. INTRODUCTION

Direct etch and liftoff are the two most popular pattern transfer processes. In the direct etch process, the polymer resist is first patterned using a lithography technique such as electron beam lithography, then the pattern is transferred to the substrate or sublayer with the resist as mask by a dry etching technique such as reactive ion etching. In the liftoff process, the film (commonly metal) is coated on the resist structure, and the film on top of resist structure is lifted off when the resist underneath is dissolved, leaving behind the film structure on the area previously uncovered by resist. Compared to direct etch, liftoff is more versatile since it can work for most metals, whereas many metals including most noble metals cannot be etched by dry etching. Positive resists are typically employed for liftoff; and if the metal to liftoff is too thick (e.g., >100 nm), a double layer stack, such as PMMA/P(MMA-MAA),[1] PMMA/LOR,[2] and high molecular weight PMMA/low molecular weight PMMA,[3] can be used to give an undercut profile that facilitates a clean liftoff. However, for lifting off some structures such as nanoscale trenches or holes, a negative resist is preferred as it offers far less exposure time than positive resist (yet a complicated double liftoff process can be utilized with a positive resist for such structures[4]).

However, liftoff using (single layer) negative resist is very challenging for two reasons: (1) the resist profile is tapered with wider opening due to electron forward scattering, which leads to film coating on the sidewall and thus makes a clean liftoff difficult; (2) common negative resists such as polystyrene[5,6] and SU-8 (Ref. 7) become cross-linked and insoluble upon exposure, and thus, a strong chemical such as a hot mixture of NH_4OH: H_2O_2: H_2O (RCA cleaning) must be used to dissolve it, which may attack the metal or sublayer. Despite the challenge, liftoff using single layer negative resist has been reported. Lim *et al*. carried out liftoff of 20 nm Cr with ma-N 2401 resist using acetone.[8] Though acetone cannot dissolve the exposed ma-N 2401, the resist was detached by prolonged ultrasonic agitation. However, as expected, the resulted Cr pattern had a rough edge. Similar rough edge was also resulted for the liftoff of Au using ma-N 1405 resist.[9] Passi *et al*.[10] achieved liftoff of Ge and Pt (both resistant to HF) with hydrogen silsesquioxane (HSQ) resist using HF, for which the application is limited since HF attacks most metals.

A double layer stack may also be used for liftoff with negative resist, but it is more limited than positive resist. For example, the popular liftoff polymer LOR (based on polydimethylglutarimide, or PMGI) may not work well with negative resist for liftoff, because PMGI itself is a positive resist[11] and thus the LOR below the developed negative resist structure (i.e., the exposed area) will be dissolved far faster than the LOR at the opening (unexposed) area. As a result, one has to resort to a trilayer structure[12] consisting of (negative) resist/hard material/polymer [e.g., resist/SiO_2/ARC (antireflection coating)] for liftoff after pattern transfer to the bottom polymer layer by dry etching. One exception is HSQ that is itself a hard mask material for polymer dry etching, and a bilayer stack of HSQ/PMMA has been employed successfully for liftoff.[13] In principle, since the sensitivity ($\mu C/cm^2$) for negative resists like polystyrene is inversely proportional to its number averaged molecular weight,[14] one can achieve an undercut profile using a bilayer with the bottom layer having a lower molecular weight (thus less sensitive). However, despite our great effort and contrary to positive resist, we were not able to find a solvent that can dissolve polystyrene for spin-coating without dissolving significantly the bottom polystyrene layer during the spin-coating of the top layer.

In this paper we will report a simple liftoff process with a single layer negative resist by low energy exposure, which resulted in an undercut profile, with an un-cross-linked or

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only partly cross-linked bottom layer soluble in common solvents. We chose polystyrene to demonstrate the process since it is a very versatile resist, for which the exposure property can be tuned simply by varying the molecular weight, and it can be thermally developed[15] as well as coated by thermal evaporation for nanolithography on nonplanar surfaces.[16,17] The key advantage of our liftoff process is obviously its simplicity; however, we were not able to achieve sub-500 nm resolution with low energy exposure.

II. EXPERIMENT AND NUMERICAL SIMULATION

Polystyrene with weight averaged molecular weight of 283 kg/mol was dissolved in chlorobenzene to give two film thicknesses of 220 and 500 nm after spin-coating. The number averaged molecular weight, which determines the resist property,[14] was 64 kg/mol, leading to a polydispersity of 4.4. As shown previously, this broad distribution would not affect substantially the resist exposure property.[14] The film was baked at 120 °C for 10 min to drive off the solvent. Next, the resist was exposed at 1–5 keV using Leo 1530 SEM equipped with a nanometer pattern generation system, and developed with xylene for 45 and 90 s for 220 and 500 nm film, respectively. Subsequently 10 nm Cr was e-beam evaporated and lifted off by soaking the sample in xylene for 10 min.

In order to obtain the electron penetration depth into the resist at low energy exposure, we carried out numerical simulation with Casino v3 (University of Sherbrooke, freely available[18]). The software is based on Monte Carlo modeling to obtain the electron trajectory in solid, and it considers the interaction and generation of x-ray and backscattered and secondary electrons. In our simulation, the trajectories of 10 000 primary electrons were simulated, from which we deduced the electron penetration depth into the resist at electron energy of 1–5 keV.

III. RESULTS AND DISCUSSION

An undercut profile (narrower opening) is essential for liftoff with a smooth pattern edge. However, as seen in Fig. 1(a), for negative resist exposed at normal condition, a tapered profile (wider opening) is typically formed due to electron forward scattering, and the longer dissolution time of the upper part of the resist than the lower part (this effect is insignificant if the resist has a high contrast for which lateral dissolution toward the less exposed region is negligible). In this study, we attempt to achieve an undercut profile using low energy exposure for which most electrons do not reach the resist bottom, as shown in Fig. 1(b). Here, the undercut at the resist bottom is owing to the very fast lateral development of the unexposed or under-exposed resist there. Figure 2 shows the developed polystyrene profile exposed at 2 and 5 keV for the 220 nm thick film, and 4 and 5 keV for the 500 nm thick film. As expected, when exposed at relatively high energy, a positively tapered profile was obtained; whereas a clear undercut profile was resulted with low energy exposure.

In order to estimate the electron penetration range and scattering volume, we utilized numerical simulation to obtain the distribution of electron trajectory. As is well known, secondary electrons (energy tens of eV), rather than primary ones (several keV), are mainly responsible for resist exposure because their energies are closer to that needed to induce a chemical reaction; and secondary electrons are generated along the path of the primary electrons. Figure 3 depicts the electron trajectories in 500 nm thick polystyrene coated on bulk silicon substrate at energy of 1–20 keV. At energy of up to 4 keV, forward scattering is significant and most electrons are stopped before reaching the substrate. At 5 keV, a significant percentage of electrons reached the film–substrate interface; and at 20 keV, most electrons penetrate deep into the substrate. The deduced electron penetration depth as a function of electron energy is shown in Fig. 4. This is in good agreement with the developed resist structure [Figs. 2(c) and 2(d)] that shows an undercut profile at 4 keV but a tapered profile at 5 keV for a film of 500 nm thickness.

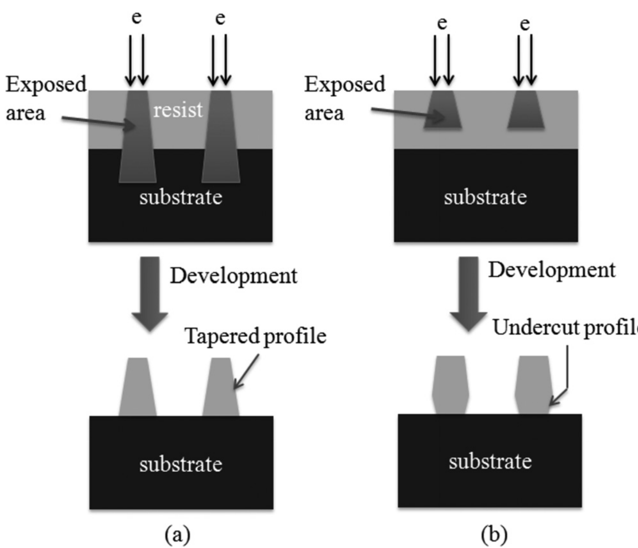

Fig. 1. Schematic diagram showing the resulted resist profile for normal high energy exposure (a), and low energy exposure with electron penetration depth smaller than resist film thickness (b). The under-cut profile for low energy exposure is due to fast lateral development of the under-exposed/unexposed resist at the bottom.

Since at low energy exposure the resist bottom part was not cross-linked or only partly cross-linked, lift-off using solvent is possible. Figure 5 shows liftoff of 10 nm Cr using xylene with 220 and 500 nm polystyrene resist. When the electron penetration depth is less than the resist thickness, such as 220 nm film exposed at 2 keV and 500 nm film at 4 keV, the liftoff was successful. But at 5 keV exposure, the polystyrene pillars for both thicknesses were not dissolved since they were cross-linked throughout the film thickness. Moreover, for low energy exposure, resist sensitivity is higher, which leads to faster writing. Lastly, since most electrons are stopped in the resist layer at low energy exposure, electron beam radiation damage to the substrate/sublayer is drastically reduced. Therefore, liftoff with the resist exposed at low energy may be utilized to fabricate metal nanostructures on top of an organic conducting layer; and we have demonstrated metallization of P3HT using a water soluble

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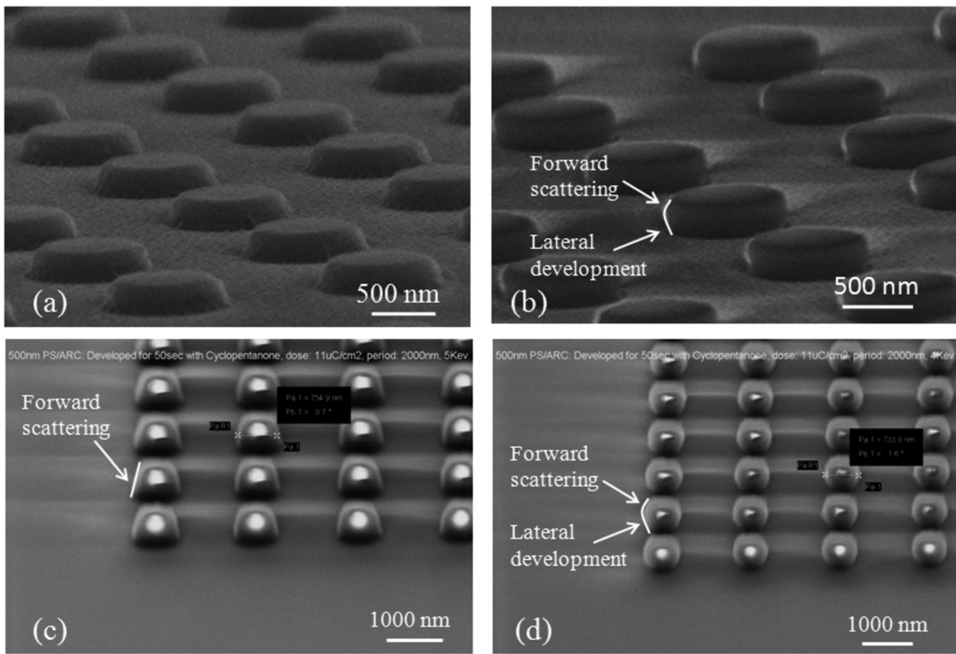

Fig. 2. SEM images of polystyrene structure exposed at (a) 5 keV for 220 nm film; (b) 2 keV for 220 nm film; (c) 5 keV for 500 nm film; and (d) 4 keV for 500 nm film. Here, the tapered profile is due to electron forward scattering, whereas under-cut at the resist bottom is due to fast lateral dissolution of the under-exposed resist there.

and developable resist poly(sodium 4-styrenesulfonate) exposed at low energy.[19]

However, with low energy exposure, we were not able to achieve regular array of polystyrene pillar structures having diameters much smaller than 500 nm, because the resist structures were found detached from or deformed and moved around on the substrate (Fig. 6). Obviously, this is due to capillary force during drying of rinsing liquid. Adhesion of

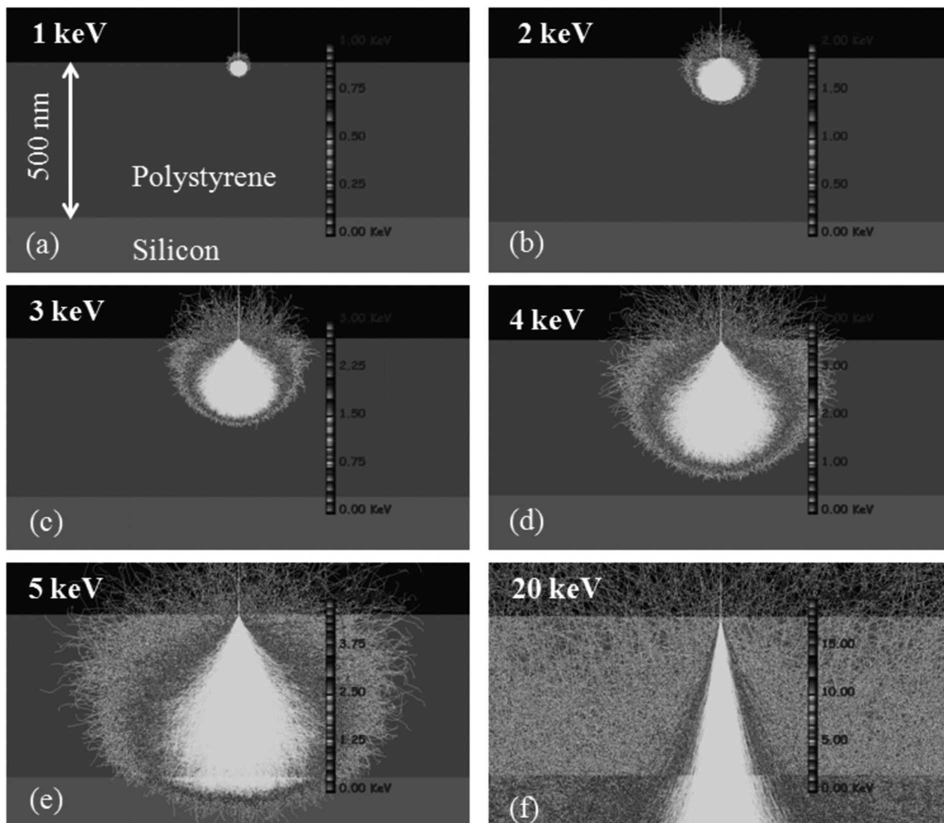

Fig. 3. Monte Carlo simulation of 10 000 electron trajectories in 500 nm thick polystyrene coated on silicon with electron energy of (a) 1 keV, (b) 2 keV, (c) 3 keV, (d) 4 keV, (e) 5 keV, and (f) 20 keV.

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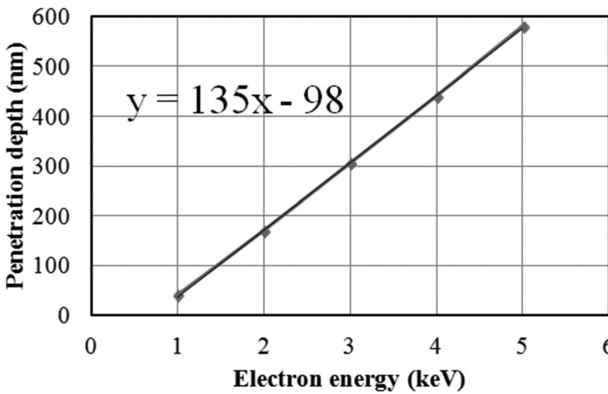

FIG. 4. Simulated electron penetration depth in polystyrene resist as a function of electron energy.

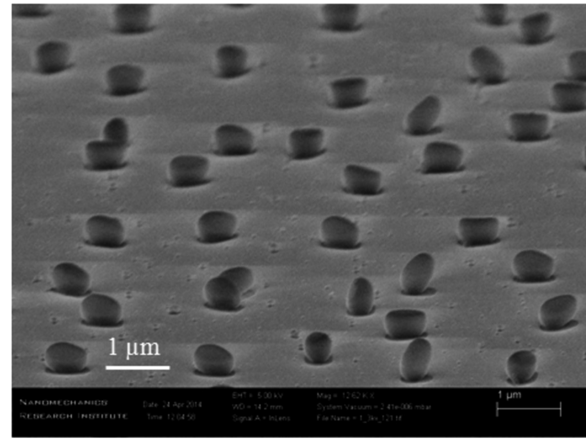

FIG. 6. SEM image of polystyrene pillars exposed at 3 keV. The film thickness is 500 nm that is larger than the electron penetration depth of 300 nm for 3 keV exposure. The designed pattern consists of 2D periodic dot array, but most pillars were detached, deformed, and moved away from its original location.

polystyrene structure to the substrate is also critical, and the adhesion must be weaker for exposure at low energy than high energy. To evaluate the effect of the development process on adhesion, it is known that development is not a layer-by-layer linear dissolution process.[20,21] Instead, the solvent diffuses and penetrates below the top (recessing) surface and dissolves or swells the resist there. The situation is worse for low energy exposure because the under-exposed resist at the bottom is more susceptible to swelling/weakening by the solvent developer that has penetrated there. The smaller pillars suffer more from capillary force, since adhesion force is proportional to d^2 (d is pillar diameter) whereas capillary force is proportional to d.

In order to verify that the solvent can penetrate through the top cross-linked layer, we exposed large squares each with an area of 400 μm^2 in 500 nm thick polystyrene, at an area dose of 50 $\mu C/cm^2$ (very high dose to ensure fully cross-linking of the top layer) and electron energies of 1–5 keV. For such large squares, lateral development would be negligible, and the pattern would detach only if the polystyrene at the resist/substrate interface is attacked by the developer that may diffuse through the top layer to reach this interface. To magnify this effect, we developed the resist in xylene for up to 45.5 min. As shown in Fig. 7, the square exposed at 5 keV survived this long development, which is because the electrons at this energy can reach the interface to fully cross-link

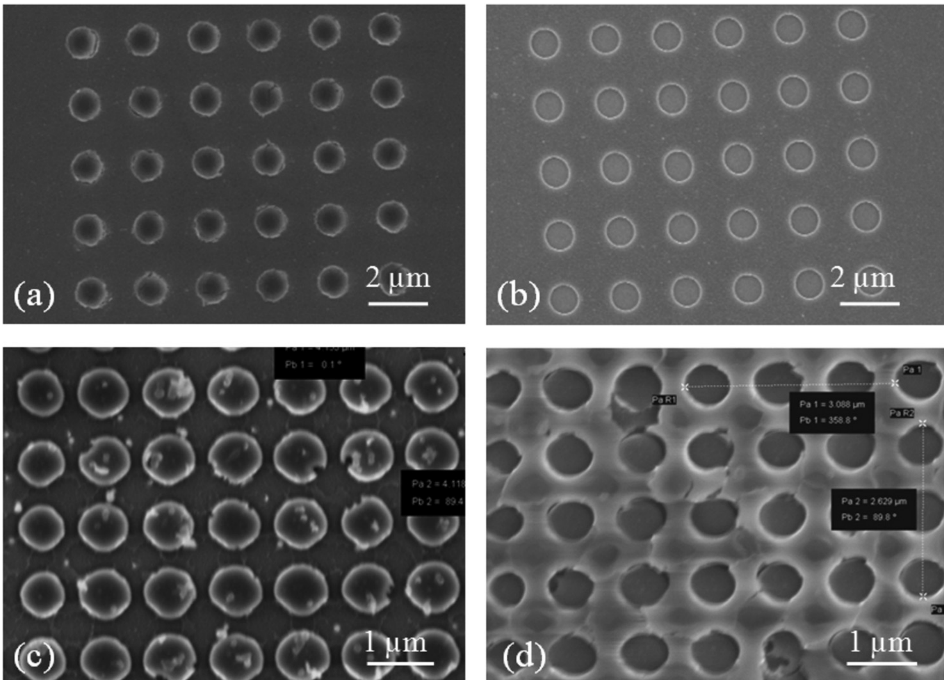

FIG. 5. SEM images after liftoff of 10 nm Cr using polystyrene resist with diffident thicknesses and exposure energies. (a) 220 nm resist exposed at 5 keV; (b) 220 nm resist exposed at 2 keV; (c) 500 nm resist exposed at 5 keV; and (d) 500 nm resist exposed at 4 keV. The liftoff in (a) and (c) was not successful (resist pillars not dissolved) because cross-linked polystyrene became insoluble in xylene.

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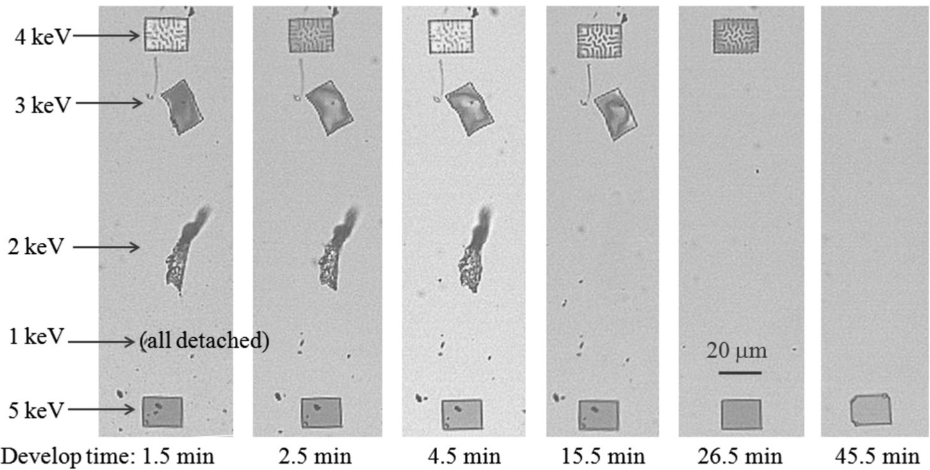

FIG. 7. Optical microscope image of large polystyrene squares after exposure at 1–5 keV and development in xylene for 1.5–45.5 min.

the resist there. For 1 keV exposure, the square was detached even after a short development time of 1.5 min. This is because the cross-linked top layer is very thin (around 40 nm, see Fig. 4) at 1 keV exposure, so the solvent developer penetrated through this layer easily. For exposure at 2, 3, and 4 keV, the squares were noticeably deformed, and they were found detached after 15.5, 26.5, and 45.5 min development, respectively. This clearly indicates that the solvent developer can diffuse to the interface and gradually dissolve the un-cross-linked or only partly cross-linked resist there.

IV. SUMMARY AND CONCLUSIONS

We demonstrated metal lift-off using negative polystyrene resist by low energy exposure. It was shown that low energy exposure led to an undercut profile which is critical for a clean lift-off. Moreover, since the resist at the bottom is not cross-linked with low energy exposure, liftoff using a common solvent was achieved. However, sub-500 nm resolution was challenging to attain using the current method due to capillary force that detached the fine polystyrene structure exposed at low energy. The effect of capillary force is more serious for low energy exposure because the developer can diffuse through the top cross-linked layer to dissolve the un-cross-linked resist at the film-substrate interface. Since low energy electrons are mostly stopped inside the resist layer, radiation damage to the sublayer is greatly reduced. Thus, the current method, when polystyrene is replaced with a negative water soluble resist, may be used to fabricate metal nanostructures on top of an organic conducting layer insensitive to water.[19]

ACKNOWLEDGMENTS

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