Area-selective atomic layer deposition of platinum using photosensitive polyimide

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Abstract

Area-selective atomic layer deposition (AS-ALD) of platinum (Pt) was studied using
photosensitive polyimide as a masking layer. The polyimide films were prepared by spin-coating
and patterned using photolithography. AS-ALD of Pt using poly(methyl-methacrylate) (PMMA)
masking layers was used as a reference. The results show that polyimide has excellent selectivity
towards the Pt deposition, after 1000 ALD cycles less than a monolayer of Pt is deposited on the
polyimide surface. The polyimide film could easily be removed after ALD using a hydrogen
plasma, due to a combination of weakening of the polyimide resist during Pt ALD and the
catalytic activity of Pt traces on the polyimide surface. Compared to PMMA for AS-ALD of Pt,
polyimide has better temperature stability. This resulted in an improved uniformity of the Pt
deposits and superior definition of the Pt patterns. In addition, due to the absence of reflow
contamination using polyimide the nucleation phase during Pt ALD is drastically shortened. Pt
patterns down to 3.5 μm were created with polyimide, a factor of ten smaller than what is
possible using PMMA, at the typical Pt ALD processing temperature of 300 °C. Initial
experiments indicate that after further optimization of the polyimide process Pt features down to
100 nm should be possible, which makes AS-ALD of Pt using photosensitive polyimide a
promising candidate for patterning at the nanoscale.

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Keywords: atomic layer deposition, platinum, area-selective deposition

(Some figures may appear in colour only in the online journal)

1. Introduction

Platinum (Pt) is of interest for many applications, due to its
high chemical stability, catalytic properties, and excellent
electronic properties. In the field of future nanoelectronics, Pt
is a promising candidate for metal contacts in field-effect
transistors because of its high work function of 5.6 eV and
low resistivity of 10.8 $\mu\Omega$ cm. For example, Pt is considered
as a contact material in carbon nanotube and graphene field-
effect transistors, where the high work function allows for the
formation of an ohmic contact resulting in a lower contact
resistance and better device performance [1, 2].

To incorporate Pt in these devices, Atomic Layer
Deposition (ALD) is a promising method. The self-limiting
nature of the ALD process allows for the deposition of con-
formal and uniform Pt thin films, with sub-monolayer control
over the layer thickness. The self-limiting and chemical nat-
ure gives ALD significant advantages over other vapor
deposition techniques when films of low thickness, high
uniformity and good conformality are required. ALD, like
other gas phase deposition techniques, has no inherent growth
control in the lateral dimension, which is desirable for
applications in nanoelectronic devices.

To overcome this issue, area-selective ALD (AS-ALD) has gained considerable scientific interest in the last few years. AS-ALD relies on the activation or deactivation of areas on the target substrate, to prevent or promote ALD precursor adsorption [3]. This results in the selective deposition of the ALD film on the desired parts of the substrate. Currently two methods have been reported to achieve area-selectivity of Pt ALD; (1) the use of self-assembled monolayers [4, 5], or thermally stable polymer films that block ALD growth [6–8], and (2) the use of an electron beam deposited seed-layer to promote Pt growth [9–11]. Here we will focus on the use of thermally stable polymer films that block the ALD growth of Pt.

Previous research by Färm *et al* has shown that poly (methyl-methacrylate) (PMMA), can be used as blocking layer for the AS-ALD of Pt [6]. PMMA can be patterned using conventional photolithography or electron beam lithography (EBL). It is rather remarkable that PMMA can be used to selectively deposit Pt features. Typical deposition temperatures used for the ALD of Pt lie around 300 °C. This temperature is well above the melting point of PMMA of 160 °C [12]. The higher deposition temperature therefore, likely results in the reflowing of the PMMA resist, ultimately limiting the feature size.

For this reason polymers with a higher temperature stability such as poly(vinyl pyrrolidone) (PVP), and poly-methacrylamide (PMAM) have been investigated as blocking layers for Pt ALD [7, 8]. Successful AS-ALD of Pt using PVP could only be achieved when Al_2O_3 was used as a seed layer for Pt growth. Without a seed layer no deposition of Pt was observed in the developed areas after photolithography. This is most likely caused by PVP residues remaining in the developed areas after the lithography process. The need for an oxide seed layer to initiate growth is undesired for applications where the Pt serves as the electrode or metal contact. PMAM AS-ALD does not require a seed layer, but the selectivity of the Pt ALD process for this polymer was only investigated up to 100 cycles of Pt ALD, insufficient to form a closed Pt film [13].

In this work, photosensitive polyimide is investigated as a masking layer for the AS-ALD of Pt. Polyimide has good temperature stability (>350 °C) and can be removed using dry chemical processing, for example by applying an CF_4–O_2 plasma [14]. The minimum Pt feature size obtainable as well as the uniformity of the Pt deposition are analyzed and compared with PMMA created Pt features. It is shown that the use of polyimide improves the minimum feature size by at least a factor of ten, limited by the resolution of the lithography tool used. In addition, due to the absence of reflow contamination using polyimide, the Pt nucleation is drastically shortened.

2. Methods

Polyimide films were prepared by spin coating on 90 nm SiO_2 coated Si (100) wafers using Polyimide HD4101 (HD MicroSystems). Before spinning the wafers were heated to 200 °C for 5 min to remove all remaining water from the surface and improve adhesion. The spin speed was 6000 rpm for 90 s. After spinning the films were baked on a hot plate for 5 min at 100 °C. Patterning of the polyimide was performed using a Karl Suss MA6 Mask Aligner (I-line, 365 nm wavelength). The exposure time was 50 s using vacuum contact mode, at a light intensity of 9 mW cm^{-2}. After patterning the samples were post-baked to 80 °C for 1 min. Development of the polyimide was performed in developer PA 401D (based on cyclopentanone) for 90 s. Rinsing was done using PA400R (based on propylene glycol methyl ether acetate). The final curing step consisted of annealing the polyimide to 375 °C for an hour in vacuum. The resulting polyimide film had a thickness of 1.5 μm, determined using a J.A. Woollam M-2000D variable angle spectroscopic ellipsometer (SE). After ALD deposition the polyimide was removed in an Oxford Instruments FlexAL reactor, using a 200 W 50 mTorr H_2 plasma for 30 min.

PMMA films were prepared by spin-coating on 90 nm SiO_2 coated Si (100) wafers using PMMA A4 950k (Micro Chem). The spin speed was 4000 rpm for 1 min. After spinning the samples were baked on a hot plate at 180 °C for 5 min This resulted in a PMMA layer thickness of 220 nm. Patterning of the PMMA films was done by EBL using a FEI Helios 650 DualBeam system, with a 30 kV e-beam and a beam current of 0.63 nA. The required patterning dose was 185–300 μC cm^{-2}, depending on the pattern size. The exposed PMMA film was developed in a 1:1 Methylisobu-tylketon: isopropyl alcohol (IPA) solution for 60 s. Rinsing was performed in IPA for 45 s. After drying the samples were stored in darkness, to prevent light-induced degradation. After ALD, the PMMA lift-off was performed by annealing at 375 °C in Ar for 30 min.

The mask design for both EBL and photolithography consisted of circles, squares and lines in the range of 1−100 μm. Pt was deposited using $MeCpPtMe_3$ as the metal source and oxygen as the co-reactant at 300 °C for 1000 cycles. This resulted in a Pt layer of 50.4 nm on a bare SiO_2 substrate, determined by SE. More details on the Pt ALD process can be found elsewhere [15, 16].

The patterned films were characterized before ALD, after ALD and after resist lift-off with a zeiss axio Imager 2 Optical microscope and a JEOL 7500 FA scanning electron microscope. The selectivity of the resists towards Pt ALD was measured by a Thermo Scientific K-Alpha KA 1066 x-ray photon electroscope (XPS). The thickness of the Pt patterns after ALD, and uniformity of the deposit was determined by energy dispersive x-ray spectroscopy (EDX) with an EDAX UMSII EDX spectrometer in combination with a SE calibrated Pt thickness series. Further details on the EDX thickness calibration can be found in the online supporting information.

3. Results and discussion

First the selectivity of the Pt ALD process was tested, by performing 1000 cycles of Pt ALD on a PMMA and
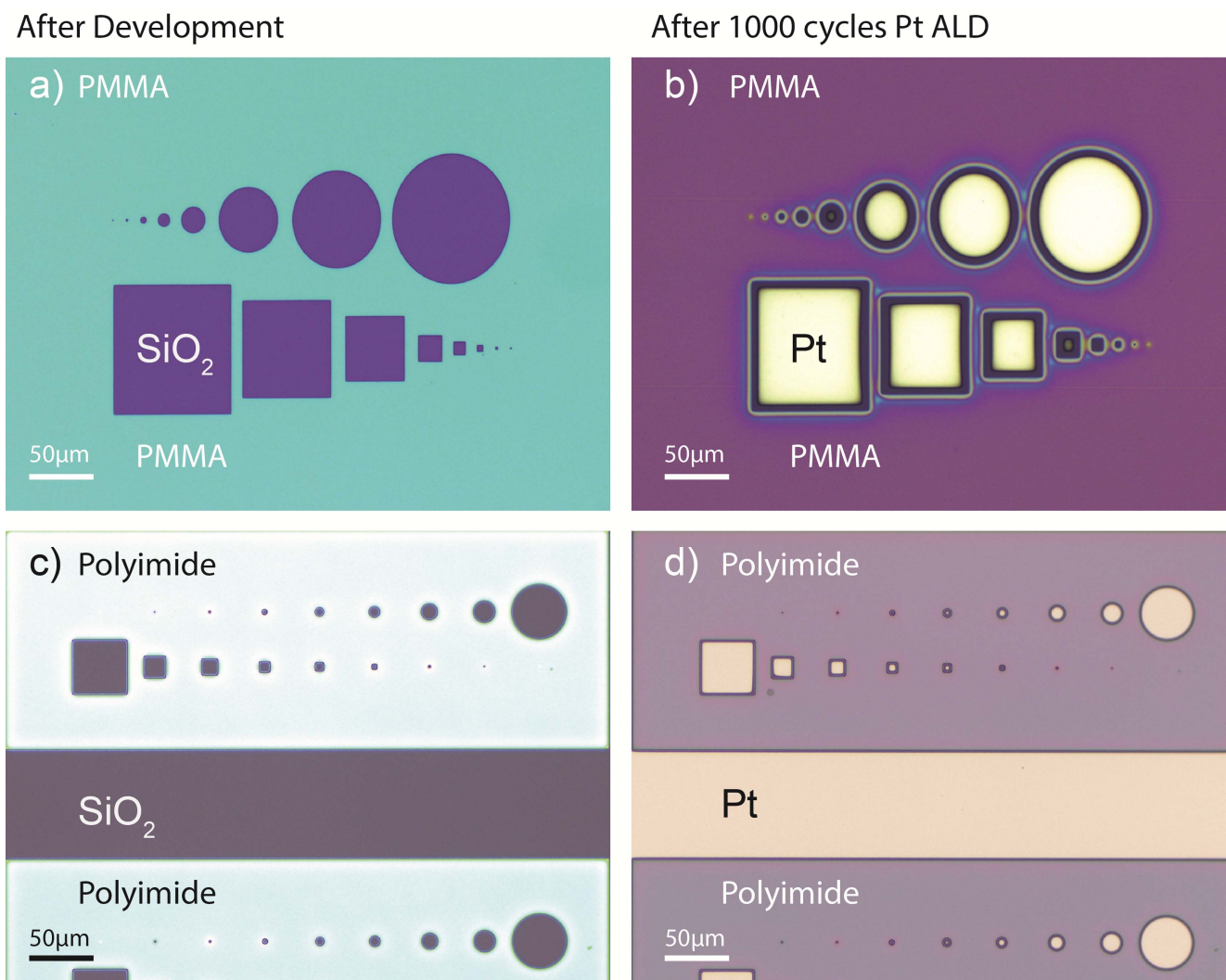
Figure 1. Optical microscopy images of (a) PMMA pattern and (c) polyimide pattern after development, and after 1000 cycles of Pt ALD without resist lift-off for (b) PMMA and (d) polyimide. The PMMA patterns range from $1-100\ \mu$m. The polyimide patterns from range $1-50\ \mu$m. The color change of the PMMA in b) towards the feature edges indicates a reduction in thickness due to reflowing during the ALD process.

polyimide layer without patterns. The amount of Pt on the resist surface after ALD was determined with XPS to be 0.06% and 0.45% for PMMA and polyimide respectively. This corresponds to less than a monolayer of Pt atoms being deposited on both PMMA and polyimide, assuming a typical XPS analysis depth of 10 nm [17]. A bare SiO_2 wafer present during the same deposition was covered with 50.4 ± 0.7 nm Pt as measured by SE, indicating that both resists provide excellent selectivity for the Pt ALD process.

To obtain an indication of the possible feature sizes and the limitations of the resists, negative patterns were created for PMMA and polyimide, as shown in figures 1(a) and (c). Positive patterns were created as well and can be found in the online supporting information, figure S3. The positive pattern helps to better visualize edge effects, for example as a result from reflowing of the resist.

Figures 1(b) and (d) show the patterned PMMA and polyimide layer after 1000 cycles of Pt ALD, before lifting off the resist. The deposition of metallic Pt is clearly visible in the

developed areas, whereas no Pt deposition is visible on the polyimide and PMMA. It can be observed that close to the PMMA edges no Pt deposition is present. The size of the edge (about $5\ \mu$m) is independent of the PMMA feature size, resulting in Pt features that are around $10\ \mu$m smaller than intended. Most likely this is caused by the reflowing of the PMMA resist at 300 °C. This assumption is supported by the change in color of the PMMA towards the feature edges in figure 1(b), indicating the resist gets gradually thinner towards the Pt feature.

The reason Pt deposition is not completely blocked over the full area by the reflowing of the PMMA resist is linked to the high molecular weight of the PMMA used (950 kg mol^{-1}). AS-ALD was also attempted using ZEP 520 A resist, but this did not result in any Pt deposition (data not shown). Compared to PMMA, ZEP 520 A has a similar temperature stability (glass transition temperature 145 °C), but a much lower molecular weight of 55 kg mol^{-1} [18]. The higher viscosity of the PMMA thus prevents reflowing to a
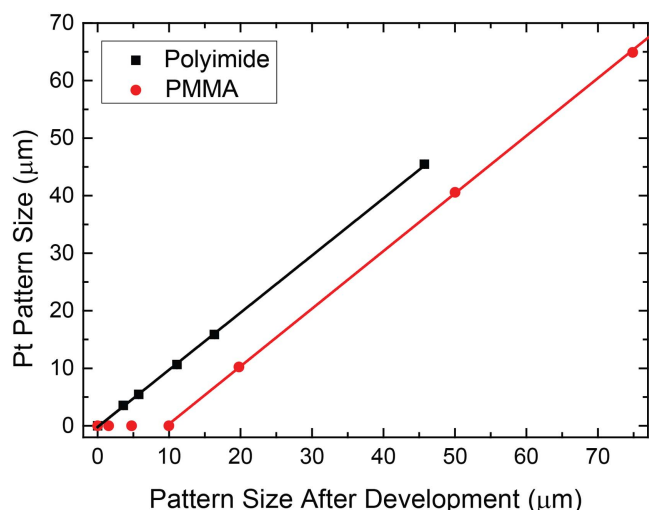
Figure 2. Pattern size analysis of the polyimide and PMMA patterns before and after 1000 cycles Pt ALD, shown in figure 1. For the polyimide the Pt pattern sizes matches the size of those present in the resist after development. For PMMA the resist openings below 20 μm contain no Pt, the deposition is blocked by the reflowing of the resist. The error bars of the measurements are <0.5 μm (smaller than dot size).

Figure 3. (a) SEM image of PMMA pattern after 1000 cycles Pt ALD and PMMA lift-off, pattern size after development: 97, 74, 49 and 20 μm. The position of the EDX line scan is indicated by the red line. The scale bar is 50 μm (b) Pt thickness determined from the EDX line scan. The scan shows that the measured feature width is smaller than intended. For the 20 μm feature almost no Pt is present.

certain extent making the deposition of Pt possible. Ultimately however, the reflowing limits the minimum feature size. Experimentally it was observed that features smaller than 10 μm contained no Pt.

The polyimide is stable to at least 375 °C, preventing reflowing of the resist during deposition. The Pt features in figure 1(d) are therefore well defined with sharp edges and can also be smaller in size when compared to the PMMA. Pt is deposited uniformly in the features and the resulting features match openings in the polyimide resist after development. This is shown more clearly in figure 2 where the dimensions of the patterns after resist development are compared with the dimensions of the Pt patterns obtained after ALD. The pattern size shown is the average of three identical patterns. The average size of the Pt patterns created using polyimide, match the opening size in the resist layer. Whereas the Pt patterns created with PMMA deviate by 10 μm, due to the reflowing of the resist.

The minimum Pt feature size using polyimide, shown in figure 1(d), is limited to about 3.5 μm. In smaller features no Pt deposition occurs, due to polyimide residue in these features, caused by overexposure of the smaller feature sizes. The polyimide thickness of 1.5 μm in combination with the lithography tool used, results in polyimide residue covering the smaller features, and thus blocking Pt ALD growth. Features with a size down to 100 nm, should however be possible. Figure S4 in the online supporting information shows the creation of small ~100 nm openings in an overexposed and overdeveloped polyimide layer. In these small openings Pt can still be deposited. This indicates that the resolution is currently limited by the polyimide lithography process. The resolution can be improved using for example a thinner polyimide film and a more advanced lithography tool.
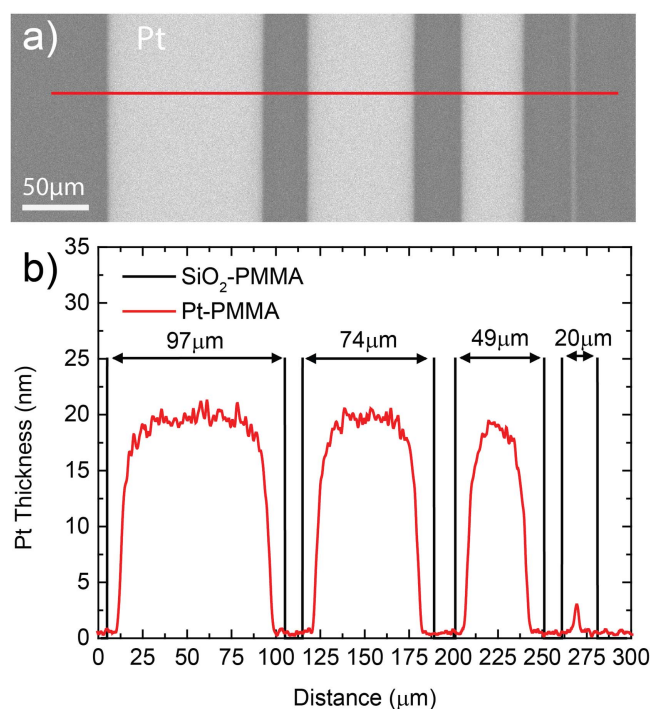
The minimum resolution of the Karl Suss MA6 mask aligner used here, in combination with an optimized resist, is around 0.8 μm.

Figure 3(a), shows a Pt pattern created using PMMA, after lift-off. The PMMA was removed by thermal annealing at 375 °C in Ar for 30 min. Thermal annealing was chosen to lift-off the PMMA instead of the more common wet-chemical approach with acetone, to prevent delamination of the Pt. The poor adhesion between Pt and the SiO_2 substrate, can lead to delamination of the Pt when solvents are used. This is especially a problem for the larger features (>50 $\times$ 50 μm).

EDX line-scans were used to get an indication of the Pt deposition uniformity (figure 3(b)). PMMA features larger than 20 μm have a thickness of about 20 $\pm$ 2 nm, which decreases slightly towards the feature edge, resulting in a slightly rounded shape of the thickness profile. For the feature of 20 μm almost no Pt is visible. Compared to the bare SiO_2 reference wafer, on which 50.4 $\pm$ 0.7 nm of Pt was deposited, the resulting Pt feature thickness is considerably less. This is possibly caused by PMMA residuals in the cleared area, in combination with the reflowing of the resist. These residues could significantly increase the nucleation delay, resulting in a reduction of the layer thickness compared to the reference SiO_2 sample [6].

Polyimide is conventionally removed using a CF_4–O_2 plasma. An O_2 plasma however can also etch or oxidize Pt [19]. To prevent this a H_2 plasma of 200 W (Ion energies <10 eV [20]) was tried instead. Using a polyimide blanket
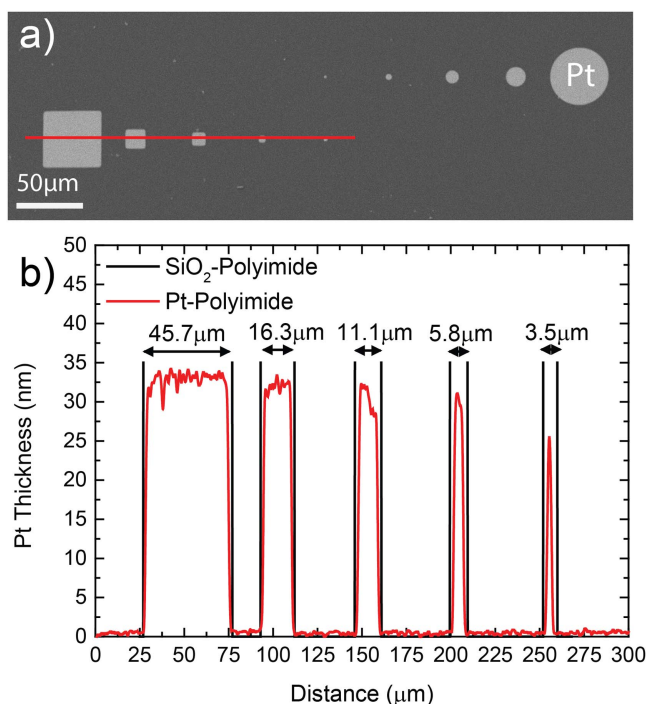
Figure 4. (a) SEM image of polyimide pattern after 1000 cycles Pt ALD and polyimide lift-off using a H_2 plasma, pattern size after development: 45.7, 16.3, 11.1, 5.8, 3.5 μm. The position of the EDX line scan is indicated by the red line. The scale bar is 50 μm. (b) Pt thickness determined from the EDX line scan.

Figure 5. SEM image of a Pt pattern for (a) PMMA and (b) polyimide after resist lift-off, the pattern size after lift-off was 46 μm. The position of the EDX scan is indicated by the red and black line, respectively. (c) Comparison of Pt thickness determined from an EDX scan for a PMMA and polyimide defined feature.

sample without deposited Pt, the etch rate was measured using SE. After 30 min of exposure no thickness decrease was observed by SE. H_2 plasma treatments of up to 2 h did not result in a change in the polyimide thickness either. This indicates that a H_2 plasma, with the conditions used here, is not able to etch bare polyimide. However, for patterned polyimide samples exposed to the Pt ALD process all poly-imide was removed after 30 min of H_2 plasma exposure, shown in figure 4(a).

To investigate if any compositional changes occurred in the polyimide film during Pt ALD, XPS measurements were performed. XPS was performed on polyimide samples after development, and after development and 1000 cycles of Pt ALD. To make sure that the oxygen half-cycle of the ALD process at 300 °C does not affect the polyimide, a polyimide sample after development and 1000 cycles of Pt ALD where no precursor was dosed in the system was used as a reference. The XPS data can be found in the online supporting info (figure S5). Deconvolution of the C1s spectrum of polyimide after development indicates that 19% of the carbon is doubly bonded to oxygen and nitrogen (C=O, C=N) and 8% is singly bonded to oxygen and nitrogen (C–O, C–N). The remainder of the C1s spectra consist of C–C bonds. No changes in the bonding configuration occurred for the O_2 reference sample, for which no precursor was dosed in the system. After 1000 cycles of Pt ALD however, the amount of C=O, C=N bonding in the polyimide decreased by 10%, and a relative decrease in the oxygen content was observed. This indicates that the Pt ALD process changes the chemical
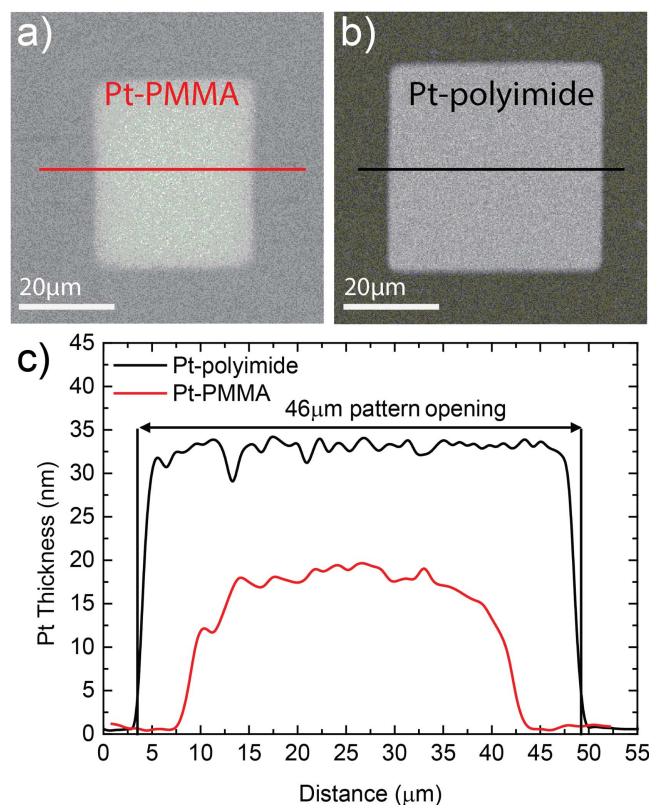
structure of the polyimide resist, making it more susceptible to etching with a H_2 plasma. Furthermore, the trace amount of Pt (0.45%) deposited on the polyimide surface after ALD, could assist the polyimide etching. Pt is a catalyst able to dissociate H_2 molecules present in the plasma and C–H and C–O bonds present in the polyimide [21].This could aid in the etching of the polyimide as well.

The EDX line-scans of the polyimide sample after lift-off in figure 4(b), show that the Pt patterns are not rounded towards the edge, as is observed for the PMMA, indicating that edge-effects do not play a role. The thickness is around 34 ± 2 nm for the larger Pt features, for the smaller features the minimum thickness is 25 ± 2 nm. This is still con-siderably less than the 50.4 ± 0.7 nm deposited on the SiO_2 blanket wafer. Possibly a small amount of polyimide residue is still present after polyimide development which increases the nucleation delay of the Pt deposition.

Figure 5 shows a direct comparison of the polyimide with the PMMA, for a positive feature of 50 μm. The PMMA feature is only 34 μm in width due to reflowing of the resist, as was observed in figure 1 as well. The Pt feature created using polyimide is 46 μm in width, and equal to the opening in the polyimide resist after development. The results show that polyimide is better suited for the AS-ALD of Pt than PMMA, due to its better temperature stability.

4. Conclusions

In this work AS-ALD of Pt was demonstrated using photo-sensitive polyimide and compared with PMMA as a blocking layer. The results showed that both polyimide and PMMA possess excellent selectivity towards the Pt precursor, resulting in less than a monolayer of ALD growth on the resists after 1000 cycles. Polyimide shows superior behavior compared to PMMA when it comes to pattern stability and definition during Pt ALD at 300 °C. The Pt patterns created using PMMA are 10 μm smaller than the initial PMMA pattern openings, due to reflowing of the resist. This limits the Pt feature size to 10 μm and above, unsuitable for many nanoelectronic applications. Pt patterns created using polyimide matched the pattern size present in the resist. The minimum pattern size obtained using polyimide was 3.5 μm and was limited by the polyimide lithography process used. Further optimization should make patterns down to 100 nm in width possible. The polyimide could easily be removed using a H_2 plasma, most likely due to a combination of weakening of the polyimide resist during Pt ALD and the catalytic activity of Pt traces on the polyimide surface. The results show that photosensitive polyimide is a good blocking layer to achieve AS-ALD of Pt for future nano-applications.

Acknowledgments

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