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SUPPLEMENTARY INFORMATION

Large area sub-100 nm direct nanoimprinting of palladium nanostructures

Mohammad S. M. Saifullah,[1*] Ramakrishnan Ganesan,[2*] Su Hui Lim,[1,3] Hazrat Hussain,[4] Hong Yee Low[5]

[1] *Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, #08-03, Innovis, Singapore 138634, Republic of Singapore*

[2] *Department of Chemistry, Birla Institute of Technology & Science, Pilani–Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, Hyderabad–500 078, Telangana, India*

[3] *Department of Electrical and Computer Engineering, National University of Singapore, 21 Lower Kent Ridge Road, Singapore 117576, Republic of Singapore*

[4] *Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan*

[5] *Engineering Product Development, Singapore University of Technology & Design, 8 Somapah Road, Building 1, Level 3, Singapore 487372, Republic of Singapore*

[*] Corresponding authors' email address: saifullahm@imre.a-star.edu.sg; ram.ganesan@hyderabad.bits-pilani.ac.in

1. Effect of heating on palladium mercaptide

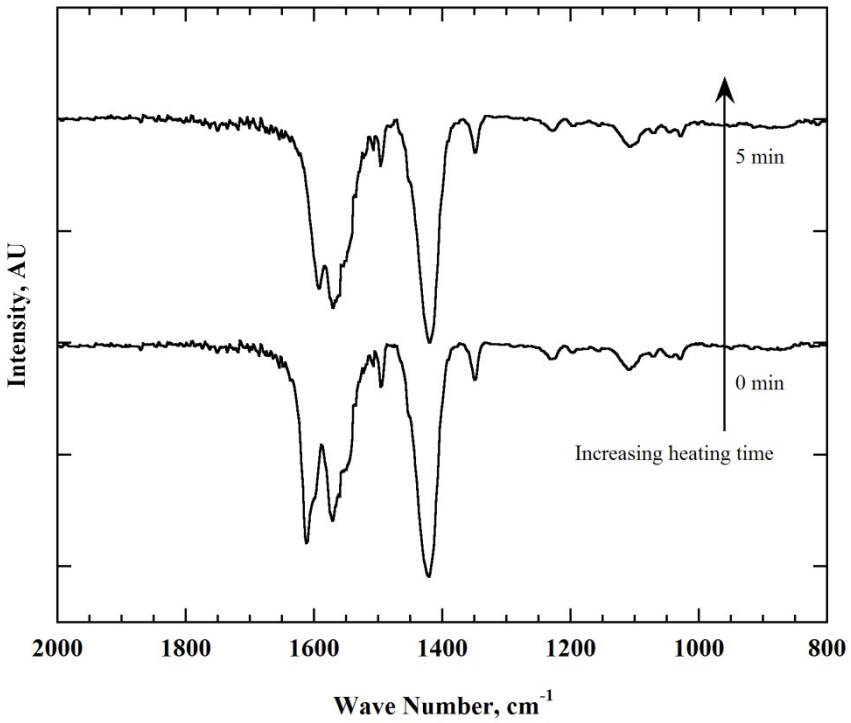


Figure 1s: FTIR spectrum showing the effect of heating palladium mercaptide film at 120 °C.

The FTIR spectrum suggests that heating palladium mercaptide (i.e., acetoxy(benzylthio)palladium) film at 120 °C for 5 minutes results in minor chemical changes such as breakdown of the benzyl mercaptide group, with hardly any effect on the acetate group. Most likely, the benzyl mercaptide molecules combine to form disulphides.

2. TGA analysis

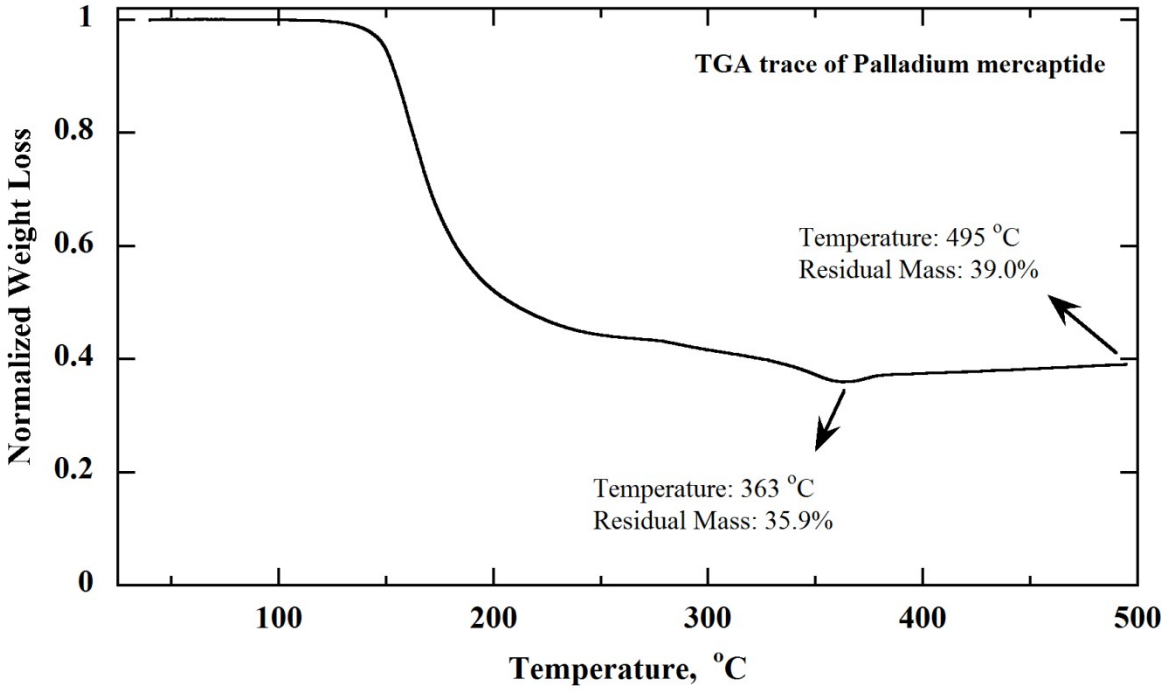
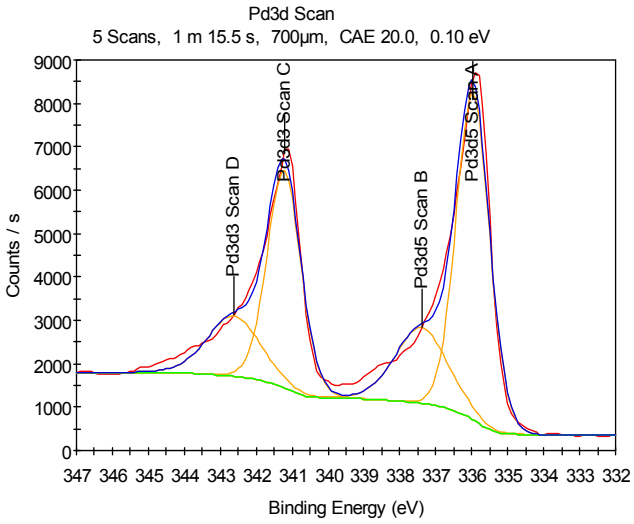


Figure 2s: TGA of palladium mercaptide in air. Notice the mass gain after the formation of palladium above 363 °C due to its oxidation.

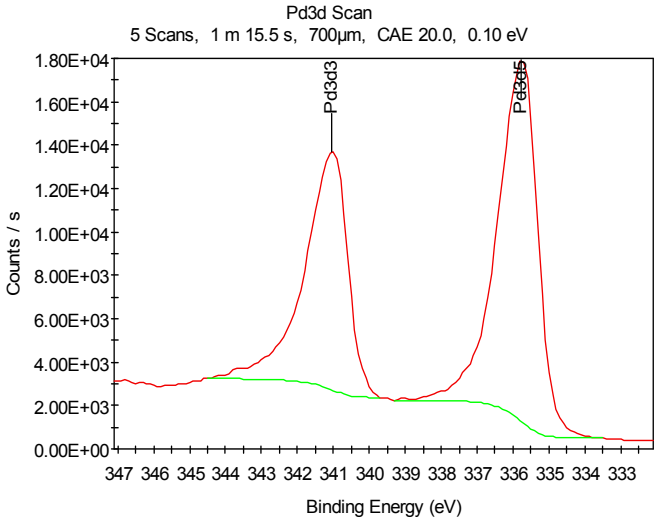
TGA study of palladium mercaptide in air suggests that palladium is the final product after the decomposition of organometallic precursor. The net remaining mass was found to be 35.9%, which corresponds closely to the theoretical metal content of 36.9% in palladium mercaptide. It is also interesting to note that heating of palladium metal above the decomposition temperature of 363 °C results in its oxidation and a steady increase in weight due to the formation of palladium oxide.

3. XPS analysis of palladium 3d binding energies

A closer look at the XPS spectrum of 3d binding energy peaks of palladium reveals the presence of oxide on the surface of palladium, as noted by the presence of a weak shoulder on 3d peaks at a slightly higher binding energy [Figure 3s(a)]. This result is consistent with earlier observation.[1]



(a)



(b)

Figure 3s: XPS study of the palladium film formed after isothermal heat-treatment of palladium mercaptide resist at 330 °C for 30 minutes (a) showing the presence of a minor shoulder at high binding energies of the palladium 3d peaks. (b) After 30 seconds of sputtering the shoulder is absent suggesting that there was indeed a presence of thin film of oxide on palladium surface.

Sputtering the surface for 30 seconds results removal of the oxide and hence the absence of shoulder [Figure 3s(b)]. Unsurprisingly, the XPS studies of palladium film heat-treated for 90 minutes revealed larger splitting of palladium 3d peaks [Figure 4s]. This is due to the higher degree of oxidation of palladium surface as compared to palladium heat-treated for 30 minutes

[Figure 3s(a)]. In this case too, argon sputtering was found to be effective to remove the surface oxide.

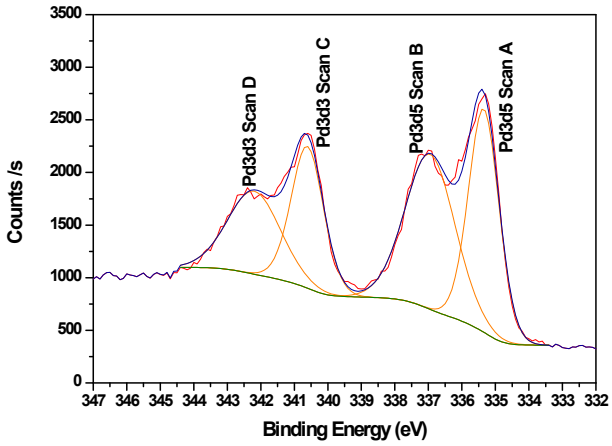


Figure 4s: XPS spectrum of 90 min heat-treated Pd film.

4. Effect of heat-treatment time

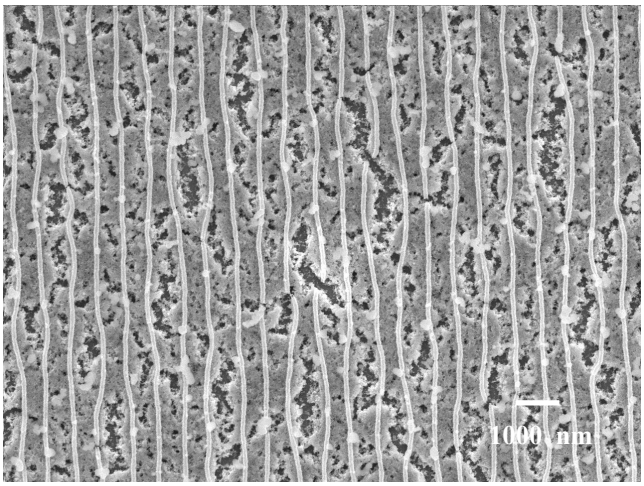


Figure 5s: SEM image of the imprinted palladium lines obtained after 90 minutes of heat-treatment when a concentrated resist formulation was used.

A palladium mercaptide resist composition with lesser amount of solvent (0.2 g of palladium mercaptide and 0.3 ml of EDMA in 2 ml of 1:3 chloroform-toluene solvent mixture) was imprinted following the standard protocol mentioned in the manuscript. Figure 5s shows the

palladium patterns obtained after heat-treatment at 330 °C for 90 min. The presence of thick residual layer and longer heat-treatment time resulted in grain growth and dewetting of the palladium film from the silicon surface, the final outcome of which is cracking of the residual layer and distortion of the imprinted lines.

5. Cross-sectional view of the as-imprinted and heat-treated patterns

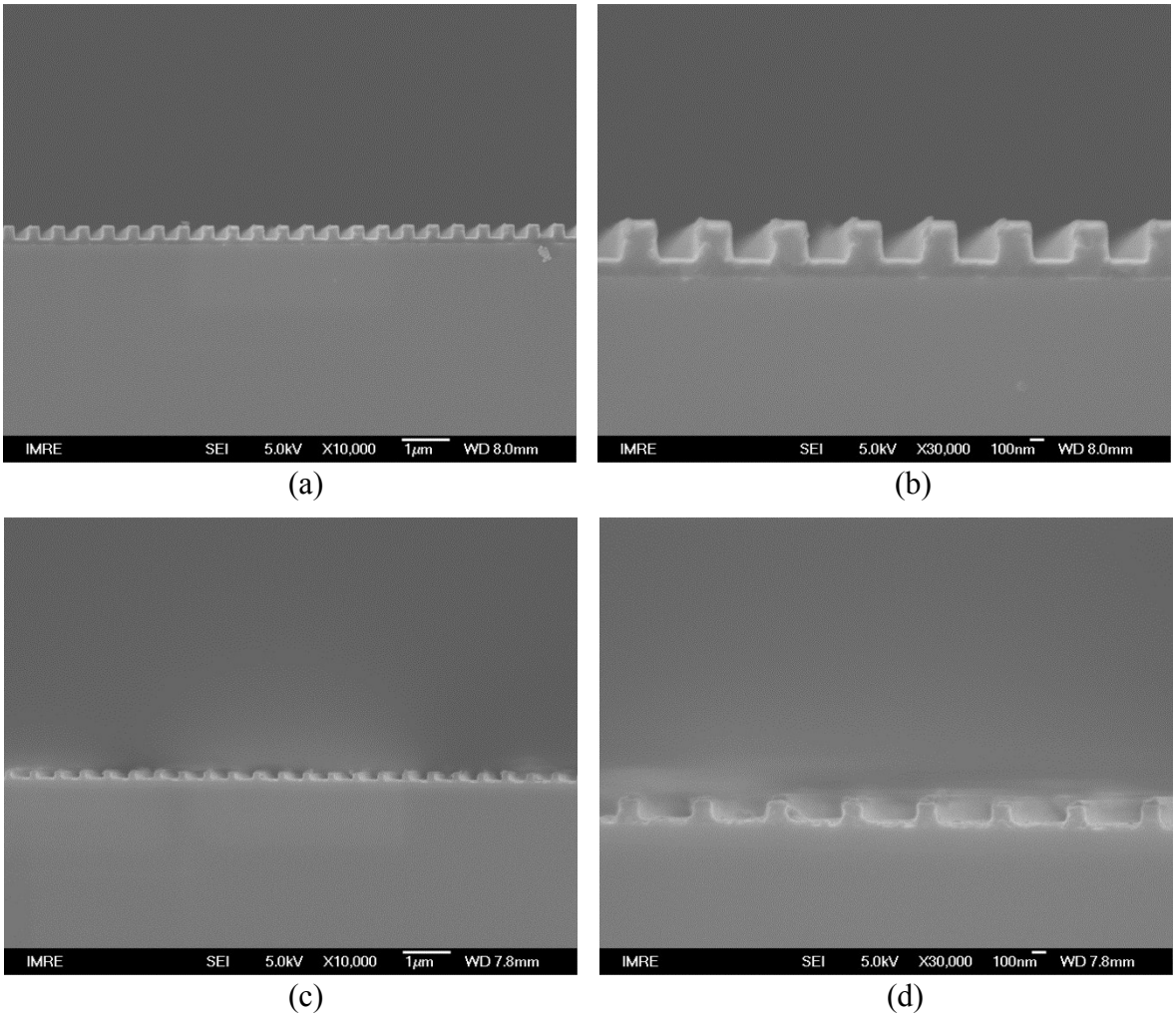


Figure 6s: SEM images of cross-section of (a, b) palladium mercaptide resist imprint made using a 250 nm mold and (c, d) after its heat-treatment using the conditions described in the paper.

References

[1] M. Peuckert, *J. Phys. Chem.* 1985, **89**, 2481-2486.