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Atomic layer deposition of nanoparticles on self-assembled monolayer modified silicon substrate

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ABSTRACT

Atomic layer deposition has attracted much attention recently in fabricating noble metal nanoparticles for a wide range of applications. We have explored synthesizing palladium nanoparticles via atomic layer deposition on self-assembled monolayers modified silicon substrate. Using alkyltrichlorosilanes as the passivating agents, our results show the method is capable of fabricating Pd nanoparticles with well controlled density and particle diameter on the modified silicon substrate.

INTRODUCTION

Noble metal nanoparticles (NPs) catalysts such as Ru, Pt and Pd play an important role in many catalytic applications due to their outstanding performance and great stability[1]. Palladium is one of the most widely used noble metal catalysts in fuel cells, automotive exhaust gas system, and so on[2-3]. Synthesizing Pd NPs with well-controlled particle size and distribution density is of great importance to optimizing their reactivity[4]. However, nanoparticles synthesized through conventional wet chemistry usually have a broad distribution of size and density, which are hard to purify[5-6]. Synthesis methods to achieve controlled size and density are urgently needed.

Atomic layer deposition (ALD) is a rapidly developing thin film deposition technique based on surface saturated chemical reactions[7-8]. Due to the self-limiting nature of half-reactions, each ALD cycle forms a single atomic layer on the substrate. This enables sub-nanometer thickness control in the vertical direction[9]. However, ALD usually could not control materials growth in the lateral direction, which is disadvantageous to nanoparticle synthesis. Through adjusting the ALD process and suitable modification of the substrates, it is possible to overcome this drawback. Recent works have shown that noble metal nanoparticles, such as Ru, Pt, Pd and their alloys have been successfully synthesized on non-flat surfaces via ALD methods[10-11].

Self-assembled monolayers (SAMs) are widely used to modify the surface properties on flat substrates include Si wafer, glass, gold and so on[12]. In previous study, it was found that the pinhole free octadecyltrichlorosilane can perfectly block the ALD growth of oxide and noble metal such as HfO_2 and Pt[13-14]. By appropriately modifying the substrate with SAMs and making use of the pinholes and defect sites on SAMs, it is possible to obtain nanoparticles with controlled size and density. In

this paper, we show that Pd NPs with controlled size and density can be obtained through ALD by tuning the SAMs growth.

EXPERIMENT

All silicon sample pieces (15×15mm^2) were cut from Si (100) substrates, and were cleaned ultrasonically by immersing in acetone and followed by anhydrous alcohol. After ultrasonication, sufficient de-ionized (DI) water was used to wash the silicon sample pieces. The wafer was subsequently immersed in H_2O:H_2O_2:NH_4OH (5:1:1) at 80℃ for 15min, then rinsed with DI water several times and dried by ultrapure nitrogen blow. The SAMs precursors we used are octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$, ODTS) and propyltrichlorosilane ($C_3H_7SiCl_3$, PTS). All the SAMs growing processes were performed in a dry, nitrogen atmosphere glovebox. Toluene was selected as the solvent with trace water eliminated. The growth time ranges from 5min to 24h. The ALD experiments were carried in a bottom heated reactor system. Ultrahigh purity nitrogen (99.999%) gas continuously passes through the chamber at 100sccm, and the reaction pressure maintained at 70Pa. Pd ALD is performed by alternately dosing Pd(Ⅱ)hexafluoroacetylacetonate ($Pd(hfac)_2$, Sigma-Aldrich, 97%) and formalin at 200℃. The $Pd(hfac)_2$ was sealed in a stainless steel bottle heated to 60℃. Formalin contains 37% formaldehyde in water with 15% methanol as stabilizer. All the lines are kept at 100℃ to avoid condensation.

The contact angle of the SAMs samples were measured by a contact angle analyzer (kino-SL200B). A field emission scanning electron microscope (FE-SEM, JSM-7600) was employed to image the Pd ALD samples. Commercially available software ImageJ 1.46 was utilized to make the statistical analysis of the particle diameter and density. The composition and binding energies were examined by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 photoelectron spectroscope (Thermo Fisher Scientific Inc.) by using the Al Kα radiation.

RESULTS AND DISCUSSION

Nucleation stage of palladium ALD process on bare Si

To investigate the early nucleation stage of Pd during ALD process, 25, 50, 100 and 200cycles of Pd ALD have been performed on bare Si wafer. Figure 1 shows the SEM images of the Pd particles grown by ALD, ~5nm NPs begin to emerge at around 25cycles. As the number of ALD cycles increase, the particles diameter rise and the interspace between the particles decrease. X-ray photoelectron spectroscopy (XPS) was used to test the 200cycles sample and results are show in the inset spectrogram of 200cycles in Figure 1(d). Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks are clearly emerged and located at 335.6eV and 340.7eV with a separation of 5.1eV which confirm the purity of metallic Pd.

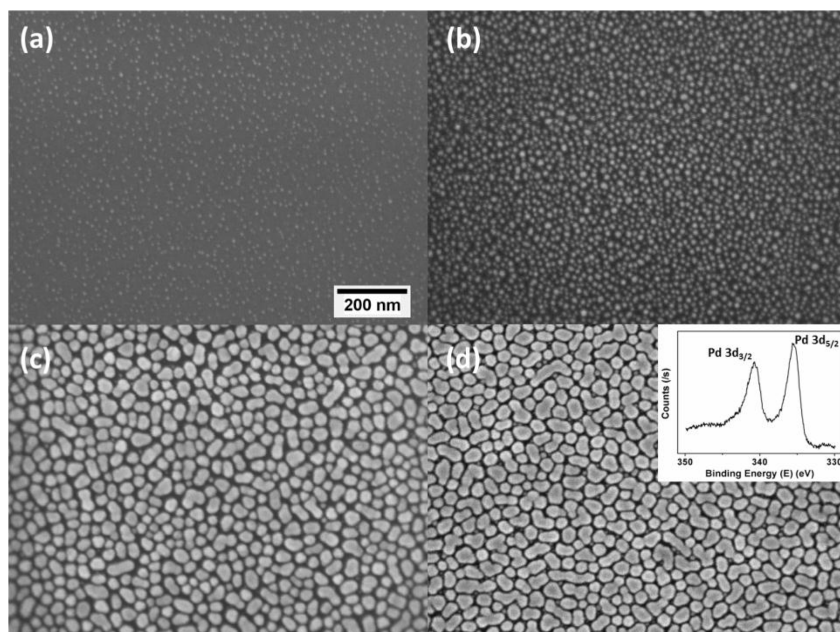

Figure 1. SEM images of (a) 25, (b) 50, (c) 100 and (d) 200 cycles (inset) XPS spectrum of Pd ALD on bare silicon substrate

The statistical analysis results about the Pd NPs density and diameter are plotted in Figure 2. The diameter of the Pd NPs increases almost linearly with the number of ALD cycles, corresponding to the ALD's circulatory growth property. The particle density increases to a maximum value from 25 to 50 cycles and then decrease as the number of cycle further increase. This phenomenon indicates new Pd sites constantly occur at the early stage to a critical point until some Pd particles merged into large islands and finally form continuous film, this kind of growth mechanism demonstrates the Volmer-Weber growth mode. The results suggest that we can synthesize Pd particles with good control of diameter by varying the ALD cycles on bare Si substrate, but it would be hard to control the particles density.

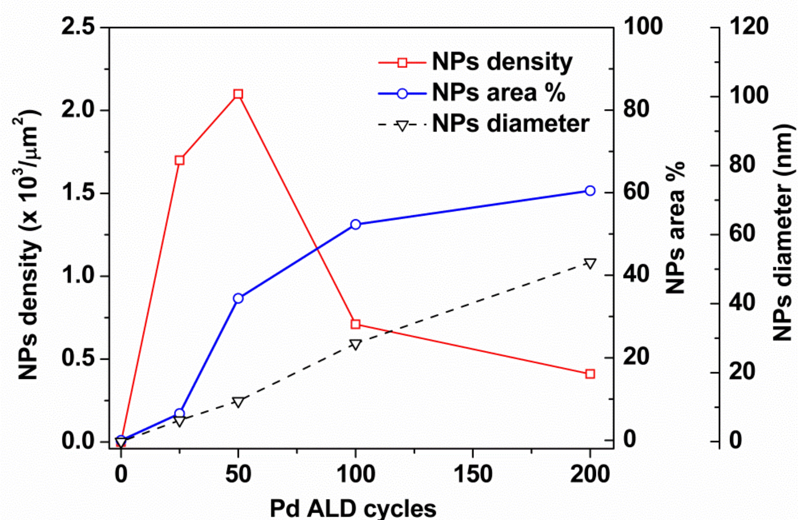

Figure 2. Pd nanoparticles density, occupied area percentage and diameter with the number of Pd ALD cycles on bare silicon wafer

The dynamic growth of self-assembled monolayers

We have studied the dynamic growth period of the ODTS and PTS SAMs on silicon wafer with different growth time. The water contact angle (WCA) increases rapidly in the first 2 to 5 hours that corresponds to a fast growth period. During this time period, large amount of the SAMs precursors physic-sorb onto the surface, making it becoming hydrophobic. Following this step comes with a much slower growth stage in which the SAMs reactants become chemical adsorbed and slowly rearrange to form a highly ordered phase. During this stage, it takes 24~48h for the WCA becoming saturated. In our experiment, the WCA of ODTS reaches a larger saturated contact angle (~108°) than PTS (~100°), indicating that ODTS SAMs has a more ordered microstructure.

Pd nanoparticles growth on SAMs modified Si substrate

Since the pinhole and defect sites of ODTS SAMs can act as active sites for ALD growth[16], we investigate the possibility of achieving controlled NP size and density utilizing pinholes and defects. This is achieved by forming a non-ideal SAM on the Si wafer using shorter dipping time and followed by a Pd ALD process. ODTS samples dipped for 0, 1, 4, 8 and 24h were used as the substrates to grow Pd NPs by ALD of 50 cycles. The statistical analysis results (plotted in Figure 3) show that the NPs size and density decrease rapidly as the growth time of ODTS SAMs increase within the first 8 hours. This time corresponds to the fast growing stage of ODTS SAMs when the SAM precursors are physisorbed on the substrate and the WCA increase rapidly.

The comparison between those data shows ODTS plays an important role in the nucleation of Pd NPs growth. The defects sites on ODTS SAMs act as the active sites for ALD growth and the other regions effectively block the deposition[15]. As a result, SAMs with long chains like ODTS has good ability to tune the particle size and density in a wide range.

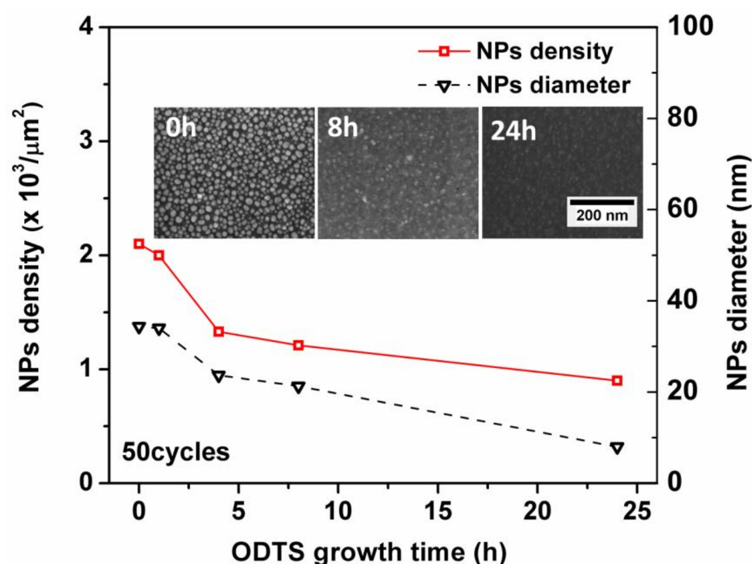

Figure 3. Pd nanoparticles density and diameter of 50 ALD cycles with ODTS growth time on silicon wafer

On the other hand, we choose another SAMs precursor PTS with shorter chain length, to investigate its ability to tune Pd NPs growth with different dip time. PTS samples dipped for 0, 1, 4, 8 and 24h were used, and the results are shown in Figure 4. From the SEM images (insets of Figure 4), the density and size of Pd NPs are almost the same on bare silicon wafer and those of PTS SAMs with different dip time. In other word, PTS SAMs has no blocking effect on the ALD growth of Pd. This phenomenon is quite different from Pd NPs grown on ODTS SAMs which the particle density and size reduce considerably as the SAMs growing. The possible reason may be that the tail group of short chain SAMs has weaker inter-chain van der Waals (VDW) attraction and is only loosely packed on the surface, different from ODTS SAMs. Thus more active defect sites are exposed on silicon substrate modified with PTS SAMs and could initiate the NP growth[16]. In contrast to ODTS, PTS SAMs with short chains seems unlikely to tune the particle size and density due to its loosely packed and disordered structure.

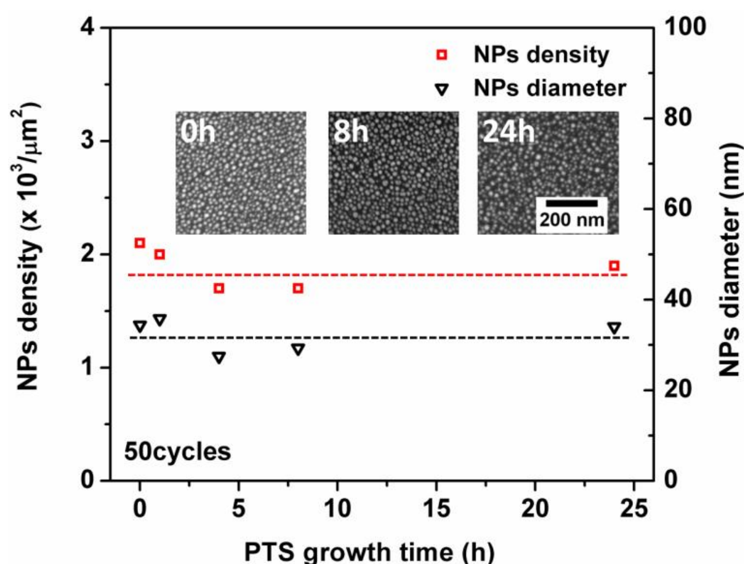

Figure 4. Pd nanoparticles density and diameter of 50 ALD cycles with vs. PTS growth time on silicon wafer

CONCLUSIONS

In this work, the early nucleation stage of Pd NPs growth on SAMs modified substrate through ALD process is investigated. Longer chain SAMs such as octadecyltrichlorosilane with different immersion time have good ability of tuning the particle size and density, where the defects sites act as the active sites for ALD growth. As a contrast, shorter chain length propyltrichlorosilane shows poor capacity to block the Pd ALD and it is ability to tune NP size and density is limited.

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