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Study on the dimensional, configurational and optical evolution of palladium nanostructures on *c*-plane sapphire by the control of annealing temperature and duration

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ABSTRACT

Metallic nanostructures can find various applications such as in optoelectronic devices, nanostructure synthesis and catalytic applications and their applicability vary depending on their size, density and configuration dependent properties. In this paper, the dimensional and configurational evolution of self-assembled palladium (Pd) nanostructures is systematically studied on *c*-plane sapphire with the control of annealing temperature (AT) and annealing duration with the initial Pd layers of various thicknesses. Depending on the AT, two distinct growth regimes are observed based on the concurrent effect of surface diffusion, surface energy minimization and Pd sublimation: i.e. (i) agglomeration of Pd nano-clusters from voids ($500 < \mathrm{AT} \leq 650\,^{\circ}\mathrm{C}$) and (ii) round nanoparticle (NP) fabrication ($650\,^{\circ}\mathrm{C} < \mathrm{AT} \leq 900\,^{\circ}\mathrm{C}$). At 950 °C, due to the sublimation of Pd atoms, substantial decrease in the NP dimension is witnessed and results in the ring patterns around the NPs. Additional investigation is performed at 950 °C to reveal the annealing duration effect on the NP evolution. Due to the dual effect of the Oswald ripening and atom sublimation, initially the dimension of NPs is grown and then gradually decays along with the duration, resulting in an inverted 'V' pattern evolution in diameter and height. Moreover, the evolution of optical properties such as absorption band and average reflectance are studied with the corresponding reflectance spectra as a function of wavelength over UV, visible and NIR region. The Raman spectra analysis depicts the variation of lattice vibration peak intensity and position based on the surface morphology of the Pd nanostructures.

1. Introduction

In the last decade, self-assembled metallic nanoparticles (NPs) have been drawing substantial research attention and adapted in various applications for the improved electronic, optical and catalytic properties [1–10]. For instance, metallic NPs can significantly enhance the photon-to-electron conversion efficiency in the UV–vis regions as extra photon absorption can be induced by the localized surface plasmon resonance (LSPR) [1–3]. Also, the precisely controlled density and diameter of semiconductor nanowires have been demonstrated on various substrates based on the outstanding catalytic capacity of metallic NPs via the Vapor-Liquid-Solid or Vapor-Solid-Solid growth mechanisms [4–6]. Over the other metallic NPs, Pd NPs exhibit an excellent catalytic capabilities and lead to the significant improvement of performance in fuel cells, water treatment, hydrogen storage and drug delivery [7–10]. The properties and applicability of Pd NPs can be highly dependent on their morphology, i.e. dimension, configuration and density, and thus, the systematical study on the evolution of Pd NP morphology can be critical and indispensable as a foundation for the massive applications based upon. At the same time, due to the high mechanical strength, chemical stability and thermal durability, sapphire can be an ideal substrate to support the Pd NPs in various fields; however, the related studies are rarely reported in literature up to date. Therefore, in this work, we demonstrate the systematical evolution of self-assembled Pd nanostructures on *c*-plane sapphire by the control of annealing temperatures with two distinct deposition amounts. The evolution of Pd nanostructures from void-layer structures to nanoclusters and round NPs is clearly demonstrated based on the systematic control of annealing temperature of a wide range for both sets. The nanostructure formation and transition are

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discussed based on the solid-state-dewetting in correlation with the surface diffusion, Volmer-Weber growth model and surface energy minimization. Further study of Pd NP formation at high temperature is performed with the variation of annealing duration to investigate the effects of Ostwald ripening, surface energy variation and Pd sublimation. Furthermore, reflectance and Raman spectral responses are correspondingly probed along with the nanostructure morphology evolution.

2. Experimental

2.1. Substrate preparation

In this work, the *c*-plane sapphire wafers with a thickness of 430 μm and ± 0.1° off-axis were utilized, iNexus Inc., South Korea. Before the fabrication, the wafers were diced into squares of $6 \times 6\,\mathrm{mm}^2$ and degassed at 600 °C for 15 min under the vacuum below 1.0×10^{-4} Torr to remove the particles, oxides and trapped air. The Raman spectrum of bare sapphire after degassing is shown in the supplementary S1 with 6 peaks that belong to the A_{1g} and E_g vibrational modes. After degassing, the morphology and surface line-profiles of bare sapphire exhibited smooth surface texture as shown in supplementary S1(a).

2.2. Sample fabrication

Deposition of Pd film is carried out by a plasma-assisted sputtering with a deposition rate of 0.05 nm/s and an ionization current of 3 mA under 1.0×10^{-1} Torr. In the temperature effect investigation, the Pd films of 12 and 35 nm thickness were deposited respectively by the precise control of deposition time. The surface morphology after the deposition of 12 nm Pd film is shown in Fig. S1. The deposited samples were mounted on an Inconel holder with an embeddable hole and transferred to a pulsed laser deposition (PLD) chamber for the sequential annealing. In the annealing process, the samples were heated from the ambient (~25 °C) to the target temperatures with a ramp rate of $4\,^{\circ}\mathrm{C\,s}^{-1}$ under the vacuum below 1.0×10^{-4} Torr. The temperature was varied between 500 and 950 °C with an equal annealing duration of 450 s at each target temperature to guarantee the sufficient surface diffusion. In the study of annealing duration, Pd film of 40 nm was prepared and annealed at 950 °C with the increasing annealing duration between 0 and 3600 s. Instantly after each growth, the temperature was lowered down to the ambient again to avoid the unnecessary Ostwald ripening.

2.3. Characterization of the experimental results

The morphology of as-fabricated Pd nanostructures was characterized by an atomic force microscope (AFM), XE-70 from the Park Systems, South Korea, with the non-contact mode. The AFM probes, NSC16/AIBS, with a length of 125 μm, width of 30 μm, thickness of 4 μm and curvature radius of less than 10 nm were utilized. The corresponding line-profiles, side-views and Fourier filter transform power spectra (FFT) were obtained by XEI software from original AFM images. The large-scale imaging was performed by a scanning election microscope (SEM), CX-200 from COXEM, South Korea and an energy-dispersive x-ray spectroscope (EDS), Noran System 7 from Thermo Fisher, USA, was utilized for the elemental characterization. The reflectance and Raman spectra were obtained at ambient by using UNIRAM II system, the UniNanoTech, South Korea, equipped with a charge coupled device (CCD). The halogen ($450\,\mathrm{nm} \le \lambda \le 1100\,\mathrm{nm}$) and deuterium ($250\,\mathrm{nm} \le \lambda \le 450\,\mathrm{nm}$) lamps were utilized as light sources for reflectance and the Raman signal was excited with a laser of 532 ± 1 nm.

3. Results and discussion

Fig. 1 shows the overall evolution of Pd nanostructures on *c*-plane sapphire by the variation of annealing temperature (AT) between 500 and 950 °C with 12 nm Pd deposition. The detailed evolution of dimension and configuration of Pd nanostructures is clearly represented by the AFM side-views, cross-sectional line-profiles and FFT power spectra as shown in Fig. 2 (Refer the supplementary Figs. S2–S4 for the large-scale AFM side-views, corresponding FFT power spectra and small-scale AFM top-views). Generally, with the increased AT, the Pd nanostructures were gradually agglomerated and evolved through two distinguished regimes: i.e. the formation of (i) voids and isolated Pd nanoclusters between 500 and 650 °C and (ii) round Pd NPs from the irregular Pd nanoclusters above 650 °C. The formation and evolution of Pd nanostructures from the uniform Pd films can be explained based on the solid-state-dewetting (SSD) [11–13]. A metallic film prepared by a sputtering at room temperature can contain higher concentration of atomic vacancies and defects, which can offer favorable sites for the nucleation at higher temperatures. When sufficient thermal energy is applied, the voids can be formed via the nucleation and expansion of vacancies at the low energy sites such as grain boundaries, triple points, pinholes, etc. in order to decrease the overall surface energy [12,13]. With the temperature is raised further, the voids can grow along with the enhanced surface diffusion of Pd atoms. The void growth rate vvoid is dependent on the temperature T and film thickness tf as [14]:

$$v_{void} \propto \frac{D_s}{T}\frac{1}{t_f^3} \tag{1}$$

The Ds is the surface diffusion coefficient, given by [15]:

$$D_s(T) = D_{s0}\exp\left(-\frac{E_A}{kT}\right) \tag{2}$$

where the Ds0 is the pre-exponential factor, EA is the activation energy for Pd on sapphire (1.56 eV) and k is Boltzmann constant (8.62×10^{-5} eV/K). First, as exhibited in Eq. (2), the Ds is exponentially related to the temperature T. The Ds can be increased by over 2 orders of magnitude in the interval between 500 and 950 °C [16–18]. Therefore, considering both the Eqs. (1) and (2), the vvoid can be positively related to theT. Thus, at increased AT, the voids can keep growing and coalesce with each other resulting in the formation of individual nanoclusters. As clearly evidenced by the line-profiles shown in Fig. 2, the agglomerated Pd nanoclusters showed a growing height with the increased AT. The transition is also confirmed with the FFT power spectra shown in Fig. 2(k) and the corresponding spectral line-profiles from the central positions as shown in Fig. 2(l). In FFT power spectra, the height information is displayed in the frequency domain by the Fourier filter transform. As the Pd nanoclusters evolved in the increasing size, the high frequency components were significantly decreased while the low frequency components increased and consequently, the distribution of frequency components tended to shrink to the near-center area along with the increased temperature as shown in Fig. 2(l). Here, the agglomeration of Pd nanoclusters is distinct from other metal elements such as Au, Pt and Cu [11,19–24]. For example, the wiggly Au nanostructures are reported in the previous works [15,19–21,25] and the formation of wiggly nanostructures may be derived from the low surface diffusion coefficient related to the insufficient energy supplement. Also, in a study of laser induced Au film dewetting, the formation of regular round nanoparticles are clearly observed in the high energy area while in the relatively lower energy area, the wiggly nanoparticles are formed instead [25]. Meanwhile, the metal nanostructure agglomeration can occur by the grain boundary grooving, typically Cu, which sharply contrast the agglomeration behavior of Au [11]. Further-