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Systematic control of the size, density and configuration of Pt nanostructures on sapphire (0 0 0 1) by the variation of deposition amount and dwelling time

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ABSTRACT

Metal nanoparticles (NPs) with controllable size, density and configuration can significantly enhance the energy conversion efficiency, detection sensitivity and catalytic activity as witnessed in various optoelectronic, optical sensing and electro-catalytic devices due to their shape and size dependent properties. In this work, we systematically investigate the evolution of the size, density and configuration of Pt nanostructures on sapphire (0 0 0 1). In particular, we have demonstrated four different configuration and evolution of Pt nanostructures with the systematic control of deposition amount (DA) based on the Volmer–Weber growth model in conjunction with the surface energy minimization mechanism, diffusion and coalescence. The various size and configuration of Pt nanostructures with respect to DA are (i) nucleation of mini-sized round shaped Pt NPs ($1 \leq DA \leq 5$ nm), (ii) growth of large sized Pt NPs ($10 \leq DA \leq 15$ nm), (iii) isolated irregular nanostructures ($20 \leq DA \leq 30$ nm) and (iv) coalesced Pt nanostructures ($DA \geq 40$). On the other hand, with the increased dwelling time (DT), irregular Pt NPs are fabricated with the increased size and improved uniformity between 0 and 450 s of annealing. The growth of Pt NPs is saturated when the dwelling time reaches the critical value between 900 and 1800 s, which can be attributed to the Ostwald ripening.

1. Introduction

Self-assembled metal nanoparticles have been widely utilized in various devices and applications including the electro-catalytic system [1–7], optoelectronics [8–10], and advanced optical sensing devices [11,12], and the size, density and even the shape of the metal NPs can affect the performance of related devices. For instance, metal particles in nanoscale size have distinctive properties due to the high surface to volume ratio compared with their bulk material and thus have been utilized as a catalyst that can significantly enhance the oxygen reduction reaction of various fuel cells [1–3]. Also, the existence of metal NPs with the characteristic localized surface plasmon resonance (LSPR) induced by the collective oscillation of the electrons can strongly enhance the energy conversion efficiency of the solar cells [8–10], and the detection sensitivity of various optical sensors [11,12]. In the meantime, due to high mechanical durability, high chemical and thermal stability (melting point of 2040 °C), sapphire has been widely utilized in various optical and optoelectronic applications such as the optical lens and as the substrates for LEDs [13–15]. As a consequence of the extensive utilization of metal nanostructures in various applications, a systematic investigation on size, density and configuration of Pt nanostructures on sapphire substrates will be desirable, which, however, is rarely reported up to now. Thus, in this work, we report the evolution of the size, density and configuration of the Pt nanostructures on sapphire (0 0 0 1) by the control of deposition amount (DA) and dwelling time (DT). With the low DA range between 1 and 30 nm, the size of NPs gradually increased whereas the density was decreased and the configuration was changed accordingly. Based on the Volmer–Weber growth model the Pt NPs were fabricated on sapphire (between 1 and 5 nm) and evolved with the vertical growth up to 15 nm and lateral growth up to 30 nm based on the surface energy minimization mechanism. Meanwhile, with the thicker Pt between 40 and 100 nm, the coalesced Pt nanostructures were observed owing to the merging

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of neighboring elongated nanostructures. In context of DT variation, between 0 and 450 s of annealing, the Pt NPs grew larger based on the Ostwald ripening. As the DT was further increased from 900 to 1800 s, the size of Pt NPs almost reach the critical value and showed a saturated behavior, namely, small change in size.

2. Experimental

2.1. Substrate preparation

In this work, the systematic control Pt nanostructures on sapphire (0 0 0 1) by the variation of Pt deposition amount (DA) and dwelling time (DT) were investigated. The substrates utilized were epi-ready sapphire (0 0 0 1) with the thickness of 430 μm and off-axis of ±0.1° from iNexus Inc. (South Korea). After being cleaved by the machine saw, the substrates were mounted on a holder and degassed at 600 °C for 15 min under 1×10^{-4} Torr in a pulsed laser deposition (PLD) system to remove the contaminants. After the degassing process, small particles on the surface was removed and the surface was ready for the Pt deposition. Figure S1 shows the AFM image of the bare sapphire surface after the degassing. The cross-sectional line-profile indicates the flat and smooth sapphire surface. Figure S2 shows the Raman spectra of bare sapphire (0 0 0 1) in which the distinctive five peaks were observed at 378.6, 416.5, 428.1, 447.1, 576, 750.1 cm^{-1}.

2.2. Sample growth

After the degassing, the substrates were introduced in an ion-coater chamber and the various thickness of Pt films (1–100 nm) were deposited by the sputtering of Pt atoms at a growth rate of 0.05 nm/s at the 3 mA ionization current under the vacuum of 1×10^{-1} Torr. The thickness of the Pt film was controlled by controlling the deposition time. The morphologies of the samples after the various deposition thickness are shown in Fig. S3 and the cross-sectional line-profiles and height distribution histograms are shown in Fig. S4. The corresponding surface area ratio (SAR) and root mean squared roughness (Rq) of the pre-annealed samples with diverse DA are summarized in Fig. S5. After the deposition, the annealing process was carried out in a PLD chamber and the substrate temperature was raised to target temperature (800 or 900 °C) at a ramping rate of 4 °C/s under 1×10^{-4} Torr. The annealing process was systematically controlled by the computer-operated recipe, and the samples were uniformly dwelt for 450 s at the target temperature to ensure the uniformity of the resulting Pt nanostructures. After the termination of each growth, the sample temperature was immediately quenched down to the ambient temperature to avoid the undesired Ostwald ripening. In order to investigate the effect of the DT on the evolution of the Pt nanostructures, the DT variation between 30 and 1800 s was carried out with the fixed DA of 10 nm and annealing temperature of 900 °C at a ramping rate of 4 °C/s.

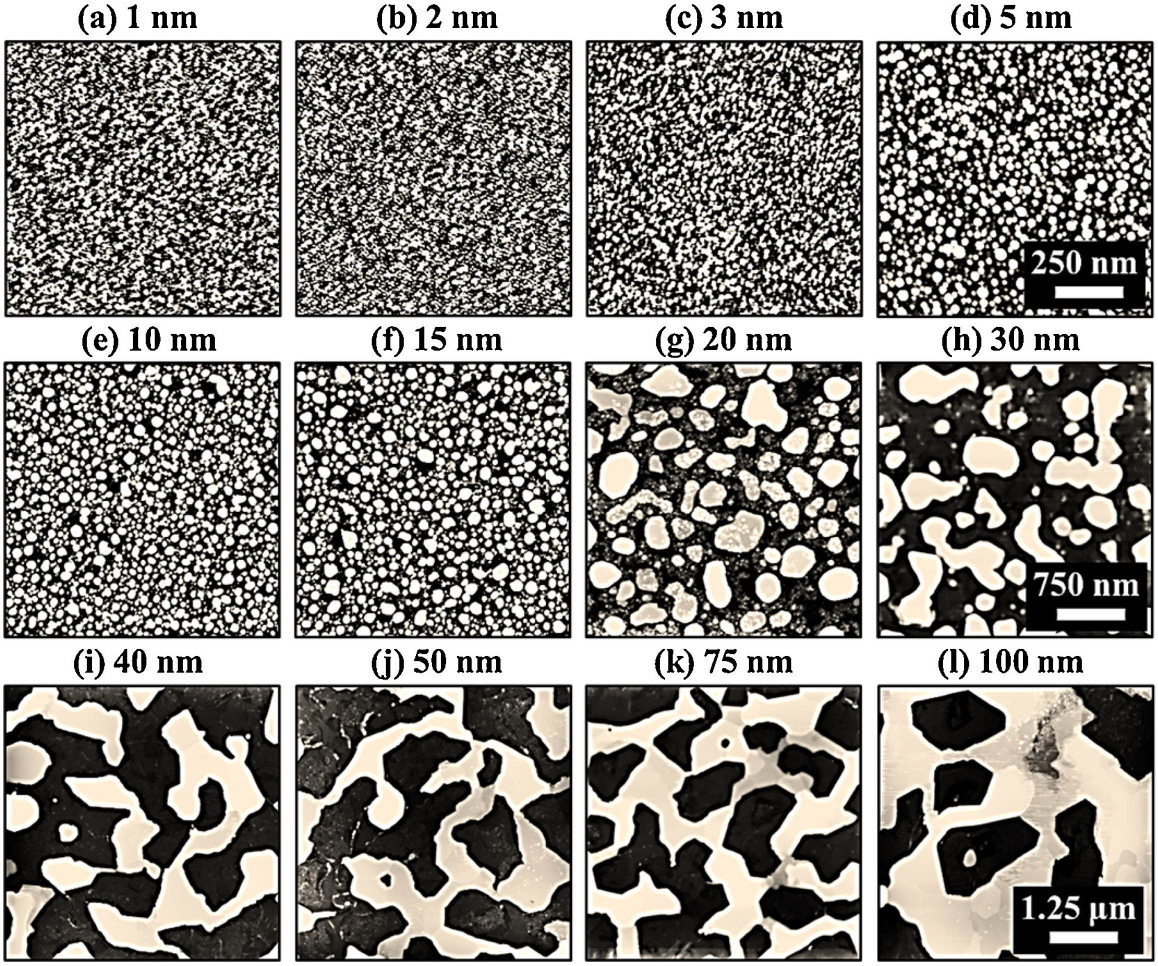

Fig. 1. Evolution of Pt nanostructures on sapphire (0 0 0 1) with the systematic variation of deposition amount (DA) between 1 and 100 nm and annealed at 900 °C for 450 s. (a)–(l) Atomic force microscopy (AFM) top-views. (a)–(d) 1 μm × 1 μm. (e)–(h) 3 μm × 3 μm. (i)–(l) 5 μm × 5 μm.