Improved localized surface plasmon resonance responses of multi-metallic Ag/Pt/Au/Pd nanostructures: systematic study on the fabrication mechanism and localized surface plasmon resonance properties by solid-state dewetting

M Sui1,2,3, S Kunwar1, P Pandey2, S Pandit2 and J Lee2,3

1 Institute of Hybrid Materials, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, People’s Republic of China
2 Department of Electronic Engineering, College of Electronics and Information, Kwangwoon University, Nowon-gu Seoul 01897, Republic of Korea
3 Authors to whom any correspondence should be addressed.
E-mail: maosui001@qdu.edu.cn and jihoonlee@kw.ac.kr

Keywords: localized surface plasmon resonance, multi-metallic nanoparticles, solid state dewetting, FDTD simulations

Supplementary material for this article is available online

Abstract

Multi-metallic nanoparticles (NPs) can offer dynamic and tunable localized surface plasmon resonance (LSPR) properties that are suitable for various catalysis, sensing and energy harvesting applications due to the wide range of tunability and applicability. In this work, the systematic fabrication and improved LSPR characteristics of multi-metallic alloy NP arrays are demonstrated based on the solid-state dewetting (SSD) of multi-layers of Ag/Pt/Au/Pd on sapphire (0001). The evolution of surface NPs in terms of configurational and elemental speciations yields vary strong and dynamic LSPR bands in the UV and VIS wavelengths based on the excitation of various plasmonic modes, i.e. dipolar (DR), quadrupolar (QR), multipolar (MR) and higher order (HO) bands, which is further exploited by the finite difference time domain simulations. Through the systematic control of multi-layer thickness, layer ratio and growth conditions, various nanostructures such as voided nanoclusters, network-like NPs and isolated semispherical NPs are obtained, which are unique in terms of morphology and elemental composition at each stage of dewetting process. The growth mechanism of multi-metallic alloy NP arrays is proposed based on the temperature driven thermal diffusion, alloying, Rayleigh-like instability and energy minimization mechanisms. Due to the subsequent sublimation of Ag atoms at above 650 °C, a sharp alteration in the elemental and morphological characteristics is demonstrated. In specific, the high percentage of Ag alloy NPs exhibits strong LSPR bands and gradually weakened along with the Ag sublimation. At the same time, however, the alloy or mono-metallic NPs without Ag still demonstrate much stronger LSPR bands as compared to the monometallic NPs by the SSD of pure films.

1. Introduction

Due to their outstanding electronic, optical and chemical properties, metallic nanoparticles (NPs) have become the fast-growing prevalent candidates in various applications such as the solar cells, LEDs, sensors, energy harvesting, imaging and catalysis [1–6]. Multi-metallic NPs, as compared with the monometallic, can exhibit superior or added properties as well as improved range of tunability and applicability due to the synergistic effect of each element [7, 8]. For example, the bi-metallic PtAg NPs exhibit the improved electrocatalytic responses for the ethylene glycol and glycol oxidation reactions due to the enhanced electronic interaction offered by the added elements [9]. The improved photocatalytic performance was demonstrated with the Au–Pt/TiO2.
composite due to the strong localized surface plasmon resonance (LSPR) of more electron-rich Au–Pt elements [10]. Further, various bimetallic alloy NPs are widely adapted for the plasmonic based photo-detectors, catalysis and sensing applications due to the superior LSPR and catalytic properties [11–14].

At the same time, the higher order tri- and quad-metallic alloy NP systems can also be of great potential candidates for various applications. Among various fabrication methods of multi-metallic alloy NPs [15–19], the solid-state dewetting (SSD) is one of the most promising techniques for the large-scale fabrication of substrate supported metallic alloyed NPs [20, 21]. Generally, the multi-metallic alloy NPs have been fabricated using colloidal synthesis and chemical reduction, which could provide superior control of NPs’ size and uniformity [22–24]. However, at the same time, many practical applications require highly pure, robust and stable NPs on the substrate and the chemically synthesized NPs possess short comings such as impurities, stability on substrate and undesired performance degradation. At the same time, the substrate patterning, e-beam lithography and nanoimprint lithography also have been implemented for the fabrication of templated assisted self-assembly of metal NPs, which generally requires highly sophisticated instrumentations and make the fabrication process very complex due to the resolution limit of lithography techniques [25]. The fabrication and detailed characterizations of various high-order multi-metallic Ag/Pt, Ag/Au/Pt and Ag/Au/Pd/Pt NPs by the SSD can be of great importance in terms of fundamental understanding and practical applications but has not been demonstrated in detail up to date.

In this work, the systematic study on the SSD of multi-metallic alloy NPs is demonstrated based on various multi-metallic thin films, i.e. Ag/Pt, Ag/Au/Pt and Ag/Au/Pd/Pt. Depending upon the multi-layer design, various size, configuration and elemental composition of NPs are demonstrated along with the systematic control of growth conditions, which is described based on the diffusion, intermixing, Rayleigh instability and energy minimization. The resulting alloy NPs with various surface morphology and elemental composition exhibit strong, dynamic and tunable LSPR properties in the UV and VIS regions and the LSPR intensity, bandwidth and peak position are closely discussed with the configuration and composition along with the finite difference time domain (FDTD) simulations.

2. Experimental section

In this experiment, the substrate of double-side polished 430 μm thick c-plane sapphire (0001) with ±0.1° off-axis (iNexus, South Korea) was first degassed in a pulsed laser deposition (PLD) chamber (DaDa TG, South Korea) at 600 °C for 30 min under 1 × 10⁻⁴ Torr in order to remove the trapped water vapors, particles and oxides. The surface morphology of bare sapphire with a surface modulation of ±0.1 nm and the corresponding reflectance and transmittance spectra are presented in figure S1, which is available online at stacks.iop.org/NJP/21/113049/mmedia. After that, the multi-layer films of Ag, Au, Pd and Pt were sequentially deposited on clean sapphire by means of plasma-assisted sputtering (COXEM, South Korea) under vacuum (1 × 10⁻¹ Torr).

Three multi-layer configurations were prepared with various individual thickness and compositions with the total thickness of 34 nm: i.e. (a) Ag₂₈/Pt₆, (b) Ag₂₂/Au₆/Pt₄, and (c) Ag₁₆/Au₆/Pd₆/Pt₆. For example, 28 nm thick Ag film was first deposited on sapphire and 6 nm of Pt layer was added atop for the Ag₂₈/Pt₆ bilayer design. The deposition sequence was chosen based on the diffusivity of metallic atoms: i.e. the diffusivity is lower on top. The deposition rate for all metal films was fixed at 0.05 nm s⁻¹ with the ionization current 3 mA: i.e. 20 s equals to 1 nm. The fabrication of various multi-metallic nanostructures was carried out by annealing at each pre-defined temperature between 500 °C and 900 °C for 120 s under 1 × 10⁻³ Torr and each target was reached at the ramping rate of 4 °C s⁻¹. The temperature range utilized was well below the melting point of all four elements and high enough to induce the dewetting of multi-layers.

For the surface morphology imaging of multi-metallic alloy nanostructures, an atomic force microscope (AFM) (XE-70, Park Systems Corp., South Korea) and scanning electron microscope (SEM) (CX-200, COXEM, South Korea) were employed. For the elemental analysis, an energy-dispersive x-ray spectroscopy (EDS) (Noran System 7, Thermo Fisher, United States) was utilized. For the optical characterization, an NOST system (Nostoptiks, South Korea) equipped with the Sr-500i spectograph, CCD detector, various optical components and combined halogen-deuterium light sources was utilized. The experimental setup for reflectance (R) and transmittance (T) spectra measurement is shown in figure S1(d). In addition, the FDTD solver (Lumerical Solutions, Canada) was performed to determine local e-field distribution and extinction spectrum of various NPs. In order to incorporate the real structure of NPs, the typical NPs from AFM images were directly imported as a simulation object. The simulation was carried out using perfectly matched layer boundary conditions in x, y, z direction and total field scattered field plane wave source in the wavelength range 250–1000 nm. The refractive index and of sapphire, Ag, Au, Pd and Pt were taken from the Palik’s and Rakic models [26, 27]. For the various bimetallic and trimetallic alloy compositions, the dielectric constant of pure metals was averaged based on the atomic % fraction [28, 29]. A mesh size of 0.5–5 nm and auto shut-off level of 10⁻⁶ were used for all simulations.
3. Result and discussion

Figure 1 shows the general fabrication process of singular and multi-metallic alloy NPs of Ag, Au, Pd and Pt on sapphire (0001) by the annealing of various multi-metallic layers. Along with the modification of annealing temperature (Ta), thickness and multilayer composition, the various surface morphology of NPs with diverse elemental composition can be formed from the continuous multilayer films. Generally, the sputter-deposited metallic monolayer or multilayer on substrate is quasi-continuous and metastable, which can dewet into the individual nanostructures upon annealing based on the SSD [30, 31]. The dewetting of thin films or formation of NPs can be initiated by the atomic diffusion and then driven by the surface and interface energy minimization [32]. The SSD of Ag/Pt bilayers or higher order alloy layers can involve additional mechanisms, as compared to a single element SSD, such as the inter-diffusion of atoms, formation of alloy, enhanced diffusion of atoms and dewetting in the alloy phase along with the sublimation of Ag atoms as illustrated in figures 1(a)–(d). In this study, the multilayer configuration was adapted based on the atomic diffusivity of metals as shown in figure 1(a) such as the diffusion coefficient of metal atoms decreases from bottom to top layers. This deposition configuration was expected to drive the dewetting process much faster than any other deposition order as the dewetting mainly depends on the underlying metal layer properties [33].
Initially, the atomic intermixing can be very likely to occur through the vacancies and pinholes at the interfaces due to the thermal activation of atoms in different metal layers. In fact, some metal pairs such as Ag and Pt exhibit large miscibility gap and variation in melting point and thus the alloy formation of AgPt at bulk phase is somewhat challenging. However, annealing of quasi-continuous nanoscale Ag/Pt bilayer at sufficiently high Ta can induce intermixing through the atomic vacancies, pinholes and grain boundaries. In the case of Ag, Au and Pd atoms, they can intermix well to form homogeneous alloy due to the complete miscibility nature [21, 34]. At increased Ta the interface between metal layers can be consumed by increased atomic intermixing and finally fully intermixed or alloyed AgPt layer can be resulted as illustrated in figure 1(b), which eventually nucleate and initiate the dewetting process. Depending upon the Ta, various growth stages can be obtained such as the voids, connected nanostructures, irregular nanostructures and dome shaped NPs as shown in figures 1(c)–(d). Meanwhile, due to the high vapor pressure of Ag, the morphological and elemental properties of alloy NPs can be largely affected by the Ag sublimation. The alloy NPs with Ag atoms formed at medium temperature completely lose the Ag atoms at high temperature and thus finally the alloy or monometallic NPs without Ag can form as shown by the typical AFM images and EDS spectra of AuPdPt alloy NPs at 550 °C and 900 °C in figures 1(c–d) and (e). The structural and elemental variation in the surface NPs directly determines the optical properties as can be seen in figures 1(f) and (g). The detailed characterization on the dewetting behavior and corresponding optical characteristics of NPs fabricated with the various Ag/Pt bilayer, Ag/Au/Pt tri-layers, and Ag/Au/Pt/Pt quad-layers composition is described in the following sections.

Figure 2 presents a detailed analysis of AgPt and Pt NPs obtained with the Ag25/Pt60 bilayers by annealing between 500 °C and 900 °C for 120 s. In contrast to the dewetting of pure Ag and Pt films [30], the Ag/Pt bilayer demonstrated distinct surface morphology of alloy NPs at low Ta as well as much improved structure of Pt NPs at high Ta. In specific, at 500 °C, the voids and grains were formed as shown by the AFM side-view in figure 2(a). The voids on films can be formed due to the coalescence of the atomic vacancies while the granular features can develop by the agglomeration of diffusing adatoms [35]. From the cross-sectional line profile, the typical void size was found to be ~30 nm in depth and ~100 nm in width. When the temperature was increased to 550 °C the voids were grown largely due to the coalescence growth and eventually the layered nanoclusters were fragmented into the irregular NPs [36] as seen in figure 2(b). The network-like irregular NPs were further fragmented and thus the isolated NPs were formed at 600 °C, which can be described by the Rayleigh-like instability and surface energy disorder of large nanoclusters [37, 38]. The average height of isolated NPs was ~100 nm while the average lateral width was sharply decreased as observed in figures 2(b) and (c). In addition, the surface evolution was also studied in terms of RMS roughness (Rq) and surface area ratio (SAR) as presented in figures 2(g) and (h). The Rq and SAR were sharply increased from 16.8 to 28.5 nm and 5.4% to 10.1% with the evolution of irregular nanoclusters between 500 °C and 550 °C.

Further increase in Ta (> 600 °C) caused the sharp transition in the NPs size and configuration. For instance, the semi-spherical NPs of ~100 nm height and 250 nm width were obtained as shown in figures 2(d–f). Similarly, the Rq and SAR were sharply reduced and remained comparable between 650 °C and 900 °C, as the average NPs size was similar. The specific value of Rq and SAR were summarized in table S1. The sharp decrement in size and surface coverage of NPs despite the enhanced dewetting at high Ta can be due to the material loss by the sublimation. Thus, to confirm the sublimation of element and variation in alloy composition, the EDS analysis was performed on each sample as shown in figures 2(i–k). As shown in the summary plot of at% of Ag and Pt, the average composition was Ag-8.32at%Pt, Ag-91.35at%Pt and Ag-100at%Pt at 500 °C, 650 °C and 700 °C respectively. At higher Ta, the composition was constant Ag-100at%Pt indicating the formation of pure Pt NPs above 650 °C. Furthermore, the EDS spectra in figures 2(i) and (k) show the distinct Pt and Ag peaks at 500 °C while only Pt peak was observed at 900 °C. (Corresponding large-scale AFM side-views, SEM images and EDS spectra are presented in figures S2–S4.) This confirmed that annealing at low Ta (<650 °C) can form the AgPt alloy NPs and annealing at higher Ta resulted in Pt NPs due to the Ag sublimation as seen in figures 1(c–d). The rate of sublimation (Rc) can increase as a function of temperature: \( R_c = (3.513 \times 10^{22}) (T/M_{Ag})^{-1/2} \times P_{eq} \), where the \( T \) and \( M_{Ag} \) are the temperature, molecular weight and equilibrium vapor pressure of Ag respectively [38, 39]. Thus, the Ag atoms can be subsequently desorbed from the alloy NPs matrix at higher Ta. After the complete sublimation of Ag atoms, i.e. between 750 °C and 900 °C, the pure Pt NPs of height ~100 nm and diameter ~300 nm were formed, which is also depicted by the minor enhancement of Rq and SAR values. While the size of Pt NPs was similar, the configuration was transformed form the irregular to the semi-spherical shape as seen in figures 2(d–f). The round shape Pt NPs can be developed due to the isotropic distribution of surface energy as well as surface energy minimization to be in equilibrium state [38].

Figure 3 shows the optical properties of AgPt alloy and Pt NPs in terms of extinction, reflectance and transmittance along with the normalized spectra. The transmittance and reflectance spectra were experimentally measured with the normal incidence of UV–vis–NIR (250–1100 nm) wavelength. The extinction spectra were determined by using the relation: \( E% = 100% - (R% + T%) \) [40–42]. The reflectance and transmittance
spectra of bare sapphire are shown in figures S1(b)–(c), which exhibit almost flat response regardless of wavelength variation between 250 and 1100 nm. Thus, the substrate influence on the LSPR properties of as-fabricated NPs can be neglected. Furthermore, the FDTD simulations on typical nanostructures were performed to access the local e-field profile and extinction power spectra as presented in figure S5. As shown in figure 3(a), the extinction spectra generally exhibited two distinct spectral behaviors depending upon the elemental composition at increasing Ta. In specific, the large and connected AgPt nanostructures between 500 °C and 650 °C showed strong absorption peaks at UV and VIS region whereas the pure Pt NPs (>650 °C) demonstrated weaker and broader peaks. Since the NPs were generally large throughout the temperature range, the absorption peaks in the UV and VIS region can be attributed to the excitation of higher order resonance (HO) and multipolar resonance (MP) modes respectively \cite{43}. The intensity of both HO and MP resonance peaks were gradually reduced with the increased Ta (up to 600 °C) as presented by the normalized extinction spectra in.

Figure 2. Evolution of self-assembled AgPt and Pt NPs on sapphire (0001) by annealing Ag$_{28}$/Pt$_{6}$ bilayer films between 500 °C and 900 °C for 120 s. (a)–(f) AFM side-views (1 × 1 μm$^2$) along with cross-sectional line-profiles. (g), (h) Plots of RMS surface roughness (Rq) and surface area ratio (SAR) with respect to temperature. (i) Summary plot of atomic (at) % of Ag and Pt at different temperatures. (j), (k) EDS spectra of the samples at 500 and 900 °C.
Figure 3. Optical properties of the AgPt alloy and Pt NPs fabricated with the Ag$_{28}$/Pt$_6$ bilayer films between 500 °C and 900 °C. (a)–(c) Extinction, reflectance and transmittance spectra of the AgPt NPs. (a-1)–(c-1) Extinction, reflectance and transmittance spectra of the Pt NPs. (d)–(f) Normalized extinction spectra. (d-1)–(f-1) Contour plots of the normalized extinction in (d)–(f).

When the relatively smaller Pt NPs were formed, the MP and HO resonance peaks were significantly attenuated as clearly displayed in figures 3(a-1) and (e), which can be correlated to the sublimation of Ag atoms from the NPs. Thus the LSPR intensity of pure Pt NP was found to be significantly weakened than the AgPt NPs. However, the resonance peaks showed mild enhancement as the size of Pt NPs were slightly increased between 650 and 900 °C as displayed in figures 3(e) and (e-1). Furthermore, the MP resonance peak width was compared for various AgPt and Pt NPs in figures 3(f) and (f-1). Generally, with the AgPt alloy nanoclusters, the broadening of MP was observed due to the LSPR dampening with the Ag sublimation. However, it was slightly narrowed with the Pt NPs at higher Ta, which can be due to the improved uniformity of Pt NPs [44]. The local e-field distribution of isolated and semispherical Pt NPs of different size was simulated as shown in figure S5, which
clearly showed the extinction maxima at different positions in the VIS wavelength. Thus, the major extinction peak in the VIS can be comprised of various plasmonic resonance modes due to the size distribution of NPs. It was also found that the e-field was strongly confined on at the interface of NPs and substrate making two strong lobes, which suggests the stronger dipolar resonance of the isolated and relatively smaller Pt NPs.

In addition, the reflectance spectra of AgPt and Pt NPs presented in figures 3(b) and (b-1), which generally exhibited two absorption dips: one at ~300 nm and another at ~460 nm by the HO and MP resonance modes of AgPt and Pt NPs as discussed. The absorption dips were gradually attenuated with the increased Ta due to the gradual sublimation of Ag atoms and evolution of pure Pt NPs in figure 3(b). Meanwhile, the absorption dip intensity can also be affected by the enhanced backscattering effect as the relatively small Pt NPs could have stronger dipolar resonance as compared to other modes. In contrast to the previous study of pure Pt NPs on sapphire [30], the reflectance spectra demonstrated the significantly enhanced LSPR responses, which can be attributed to the formation of much improved configuration and uniformity of Pt NPs.

The corresponding transmittance spectra of AgPt alloy and Pt nanostructures are presented in figure 3(c). It also clearly exhibited the distinctive LSPR response depending upon the size and elemental composition of NPs at various temperatures. In specific, the large and connected AgPt nanostructures showed flat transmittance spectra, which could be likely due to the pronounced forward scattering by larger AgPt nanostructures [45]. For the large nanoclusters, the forward scattering effect can be much stronger due to the pronounced quadrupolar resonance as compared to other modes. Along with the gradual evolution of smaller Pt NPs at high Ta, the weak absorption dips were developed at UV and VIS region as shown in figure 3(c), which can be due to the increased backward scattering as the small size NPs can have stronger dipolar resonance. This was also suggested by the reflectance spectra in figure 3(b). In terms of average reflectance and transmittance, they showed the opposite trend due to the average surface coverage behaviors: i.e. large surface coverage sample shows high reflectance and low transmittance and vice versa.

Figure 4 shows the growth of various AgAuPt trimetallic and AuPt bimetallic nanostructures on sapphire (0001) with the Ag22/Au6/Pt6 tri-layers by the variation of Ta between 500 °C and 900 °C. Although the total thickness of tri-layers was identical with the previous set, the morphological evolution of nanostructures was drastically varied. With the addition of new metallic layer, i.e. 6 nm Au in between 22 nm Ag and 6 nm Pt, the dewetting characteristic were significantly altered, which resulted in unique shape and size of NPs at a specific temperature. The tri-layers deposition was Ag, Au and Pt in a sequence from bottom to top layer according to the increased surface energy and decreased diffusivity as discussed in figure 1[46]. Upon annealing, the simultaneous interdiffusion between Ag-Au atoms and Au–Pt atoms is expected at Ag/Au and Au/Pt interfaces. Thus, the dewetting process can also be altered form the previous case due to the variation in constituent atoms and their diffusivities. Nevertheless, the adequate annealing of Ag/Au/Pt tri-layers can induce the significant intermixing and alloying of Ag, Au and Pt atoms to form various trimetallic alloy nanostructures. In specific, the evolution of widely connected and irregular AgAuPt nanostructures was obtained between 500 °C and 600 °C as shown in figures 4(a)–(c). As compared to the previous set, the dewetting extent was significantly reduced due to the lowered Ag component along with the added Au layer. This can be correlated to the low diffusivity of Au atoms as compared to the Ag as well as the interdiffusion at two different interfaces. The average height of AgAuPt nanostructures was gradually increased whereas the lateral size was decreased due to the compact agglomeration of atoms. The Rq and SAR of the corresponding samples were also increased as shown by the plots in figures 4(g) and (h) with the evolution of AgAuPt nanoclusters.

Similar to the previous set, the dewetting of alloy nanoclusters were simultaneously affected by the Ag sublimation as depicted by the decreasing at % of Ag between 500 °C and 650 °C in figure 4(i). At higher Ta, the at% of Ag was zero whereas other elements showed constant at% between 650 °C and 900 °C. The EDS spectra of samples annealed at 500 °C and 900 °C are shown in figures 4(j) and (k), which clearly indicates the Ag sublimation. Specific atomic compositions and EDS results of each sample are presented in figure S7. Between 750 °C and 900 °C, the nanoclusters were transformed into the spherical shape as shown in figures 4(d)–(f), which can be again correlated to the surface energy minimization and equilibrium configuration of NPs [37]. In this temperature regime, the Ag atoms were already sublimated, and the evolution of NPs can be attributed to the diffusion of Au and Pt atoms. The size of NPs was ~180 nm in height and ~250 nm in diameter, which was generally larger as compared to the Pt NPs from the previous set. The Rq and SAR also showed similar values at high Ta as the overall height and surface area was minorly varied.

Figure 5 shows the LSPR properties of AgAuPt and AuPt alloy nanostructures fabricated with Ag22/Au6/Pt6 tri-layers. As compared to AgPt and Pt NPs in the previous set, these NPs demonstrated distinct LSPR properties due to the variation in the surface morphology and elemental compositions. As seen from the extinction spectra in figures 5(a)–(a-2), two distinct absorption peaks were observed at UV and VIS regions, which can be induced by the HO and MP resonance modes respectively as the alloy NPs were generally larger as discussed [43]. In specific, the connected AgAuPt nanoclusters between 500 °C and 600 °C demonstrated a narrow UV absorption peak and relatively wider VIS absorption peak. As compared to the AgPt nanoclusters in the previous set, these
LSPR peaks were relatively weaker and broader as can be correlated to the reduced Ag amount. As the Ag atoms were gradually sublimated from AgAuPt alloy NPs with temperature, the LSPR peaks were further attenuated and gradually became much broader as shown in figure 5(a-1). With the formation of AuPt NPs above 650 °C, the LSPR peaks were further weakened and blue shifted as shown in figure 5(a-2). However, a mild enhancement was found in the LSPR intensity at higher Ta likely due to the size enhancement of the AuPt NPs. The LSPR peaks of AuPt NPs were found to be slightly stronger than Pt NPs in the previous set, which can be attributed to the contribution of Au component. Furthermore, the MR peaks were generally narrowed with the increased annealing as presented in figure 6(a-3) due to the improved uniformity of alloy NPs [44]. The e-field distribution of the typical AuPt NP also shows the strong confinement of e-field at NP/sapphire interface as shown in figure 5(e). The simulated extinction power spectra and e-field vector plots are included in figure S9. In the simulated extinction power spectra, the extinction maxima were observed in the VIS wavelength, which was much broader as compared to the pure Pt in the previous set. The e-field vector plot showed multiple polarities indicating the presence of different resonance modes.

The corresponding reflectance spectra in figure 5(b) exhibited a distinct spectral response as compared with the previous set. In specific, the AgAuPt nanostructures demonstrated two absorption dips at UV and VIS regions due to the HO and MP resonance modes respectively. It was also observed that the absorption dips were gradually reduced with the Ag sublimation as shown in figure 5(b-1). At high Ta, the AuPt nanostructures had much weaker absorption dips as shown in figure 5(b-2). The reduction of absorption dip intensity can also be correlated to the enhanced backscattering with the stronger dipolar resonance by the isolated and smaller AuPt nanostructures as discussed [46]. Furthermore, the transmittance spectra of corresponding nanostructures are presented in figures 5(c)–(c-2). The spectra were generally flat with the larger AgAuPt nanostructures, which can be attributed to the enhanced forward scattering by the trimetallic nanostructures. But with the evolution of

Figure 4. Growth of various AgAuPt trimetallic and AuPt bimetallic nanostructures on sapphire (0001) with Ag22/Au6/Pt6 tri-layers by the control of annealing temperature between 500 °C and 900 °C for 120 s. (a)–(f) AFM side-views (1 × 1 μm) and cross-sectional line-profiles. (g), (h) Plots of Rq and SAR. (i) Plots of Ag, Au and Pt at% as a function of annealing temperature. (j), (k) EDS spectra of samples at 500 °C and 900 °C.
isolated and regular AuPt nanostructures at high annealing temperature, the formation two weak absorption dips were realized in the UV and VIS wavelengths as shown in figures 5(c) and (c-2). In addition, along with the decreased surface coverage, the average reflectance was gradually increased while the average transmittance was decreased as shown in figures 5(b-3)–(c-3).

Figure 6 shows the fabrication of multimetallic alloy NPs by the SSD of Ag16/Au6/Pd6/Pt6 quad-layers at the identical growth conditions as in the previous sets. The overall quad-layers thickness (34 nm) was the same as the previous sets but the thickness of Ag film was further reduced whereas the Pd layer was added and thus the overall dewetting process was reduced further [46, 47]. This can be due to the reduced thickness of high diffusivity Ag while adding the low diffusivity Pd film. Furthermore, due to the increased disparity between metal atoms the intermixing process can be slowed down at different interfaces: i.e. Ag/Au, Au/Pd and Pd/Pt.
Nevertheless, annealing at sufficient high Ta could lead to the formation of completely intermixed of alloyed layers as described previously. Thus, the dewetting stages were generally common as in the previous sets but the surface morphology and elemental composition were drastically varied at specific temperatures. As shown in figure 6(a), the annealing of quad-layers films at 500 °C demonstrated the formation of relatively small and less number of voids as compared to the previous sets. The suppression of dewetting degree was clearly observed, which can be correlated to the reduced Ag and added Pd component. Consequently, annealing between 550 °C and 600 °C resulted in the formation of enlarged voids and connected AgAuPdPt nanoclusters as shown in figures 6(b)–(c). The average height of nanoclusters was gradually increased with temperature as presented by the corresponding line-profiles. Furthermore, the Rq and SAR in figures 6(g)–(h) also showed gradually increasing trend due to the increment in average height and surface area. The morphological evolution of nanostructures was also shown by the Fourier filter transform (FFT) power spectra as insets in figures 6(a)–(f). Generally, with the narrower height distribution of nanostructures at increased Ta, the FFT power spectra became smaller. In addition, the EDS analysis was performed to evaluate the elemental composition of nanostructures at specific Ta. The EDS spectrum in figure 6(j) clearly shows the presence of Ag, Au, Pd and Pt in alloy nanocluster. The summary of at% is presented in figure 6(i) while the detailed EDS spectra and elemental composition are presented in figures S12–S14. Furthermore, the detailed elemental analysis of the AgAuPdPt

Figure 6. Fabrication of multimetallic alloy NPs by the SSD of quad-layer Ag16/Au6/Pd6/Pt6 films at various annealing temperature as labeled. (a)-(f) AFM top-views of 5 × 5 μm². (a-1)–(f-1) Magnified AFM color-coded side-views (1 × 1 μm²) and cross-sectional line-profiles. (g), (h) Plots of Rq and SAR. (i) Summary plots of at % of Ag, Au, Pd and Pt. (j), (k) EDS spectra of samples at 500 °C and 900 °C.
alloy nanoclusters was performed with the sample annealed at 550 °C as shown in figures 7(a)–(g). The SEM images and elemental color maps of Ag, Au, Pd and Pt clearly show the homogeneous distribution of elements in the nanoclusters. The EDS line profile through nanocluster region also exhibited uniform distribution of Ag, Au, Pd and Pt as shown in figure 7(g). This clearly indicates that the elements are evenly distributed in the nanoclusters, which can be further improved at higher temperature. The Ag atoms were largely sublimated between 500 °C and 600 °C as shown by the decreased at%. Above 600 °C, the at% of Ag was zero while other metals were almost similar.

Once the Ag atoms were completely sublimated, the dewetting at higher temperature can be governed by the diffusion of the rest of Au, Pd and Pt atoms. Consequently, the connected AuPdPt nanostructures were gradually fragmented into the isolated nanoclusters up to 800 °C based on the Rayleigh instability as shown in figures 6(d)–(e). Finally, with the enhanced diffusion of atoms, the round AuPdPt NPs were formed at 900 °C as shown in figure 6(f). As shown in figures 7(h)–(n), the Au, Pd and Pt atoms were homogeneously intermixed to form trimetallic alloy NPs. From the EDS phase maps and line profiles, there was no contrast change or elemental inhomogeneity for Au, Pd and Pt while Ag was not detected. This again confirms that isolated AuPdPt trimetallic alloy NPs were formed at high Ta. The AuPdPt NPs were gradually increased in size at increased Ta as clearly shown by the cross-sectional line-profiles. Similarly, the Rq was gradually increased with the increased Ta based on the height increment of NPs while the SAR was increased from 500 °C to 750 °C and start to decrease at high Ta due to the reduced NPs density. The FFT power spectra were also gradually become smaller along with the increased Ta up to 900 °C, which signify the improved uniformity and reduced height distribution of nanostructures. As compared to the AuPt NPs in the previous set, the AuPdPt NPs possessed smaller vertical height but larger lateral size.

Figure 8 shows the optical properties of various multi-metallic alloy NPs fabricated with the Ag16/Au6/Pd6/Pt6 quad-layer films. As compared with previous sets, this nanostructures were larger and possessed wider surface coverage due to the relatively thinner Ag films and slower dewetting rate, which exhibited distinct optical behaviors. In specific, the pronounced UV and VIS extinction peaks were observed.
with the AgAuPdPt ($<550\,^\circ\text{C}$) and AuPdPt ($>600\,^\circ\text{C}$) NPs corresponding to the HO and MP resonance modes as shown in figures 8(a)–(a-2). As the Ag content was reduced from the previous set with the addition of Pd, the LSPR peaks were further attenuated as compared to the AgAuPt and AuPt NPs in the previous set. Similar to the previous sets, the LSPR intensity was gradually decreased with the Ag sublimation and size decrement with temperature as shown in figures 8(a-1) and (a-2). With the gradual decrement average size of AuPdPt nanoclusters up to $900\,^\circ\text{C}$, the LSPR intensity was gradually decreased.

The simulated e-field distribution of typical AuPdPt NP is shown in figures 8(d)–(e) and corresponding extinction power spectra is presented in figure S15. From the simulation, the extinction was found to be much broader than the previous sets and the extinction maxima were also observed in the UV and VIS region corresponding to the excitation of HO and MP resonance bands. The e-field vectors plots at VIS wavelength also showed the multiple vector direction as shown figure 8(e). In addition, the reflectance spectra in figure 8(b) showed absorption bands in the UV and VIS region. These absorption dips were much stronger as compared to the previous sets likely due to the large size of nanostructures. As the Ta was varied between $600\,^\circ\text{C}$ and $900\,^\circ\text{C}$, the absorption dips were gradually weakened and narrowed as shown in figure 8(b-1) along with the reduced size distribution of AuPdPt nanostructures [38]. Furthermore, the transmittance spectra of this set generally revealed the flat spectral response for the nanostructures between 500 and $900\,^\circ\text{C}$. This indicates the strong forward scattering with the large size AgAuPdPt and AuPdPt nanostructure, which could be due to the strong quadrupolar resonance as discussed. In terms of average reflectance and transmittance, this set also showed similar behavior as in the previous sets.

**Figure 8.** (a)–(c) Extinction, reflectance and transmittance spectra of various multi-metallic alloy NPs fabricated with the Ag$_{16}$/Au$_{6}$/Pd$_{6}$/Pt$_{6}$ quad-layer films. (a-1)–(a-2) Normalized extinction spectra of AgAuPdPt NPs. (b-1) Enlarged dip region in the reflectance spectra. (d) AFM image of AuPdPt NP at $900\,^\circ\text{C}$. (d-1) Cross-sectional line profile. (e) E-field profile in x-, y-plane at specific wavelengths. (f) E-field vector plots.
4. Conclusions

In summary, noble (Ag, Pt, Au, Pd) multi-metallic alloy nanostructures have been successfully fabricated on sapphire (0001) and a systematic fabrication process of employing SSD has been demonstrated to control the morphology, size and composition of various metallic alloy NPs and their optical properties. Specifically, three different multi-layer films with identical total thickness were studied under identical growth conditions at a various temperature between 550 °C and 900 °C: i.e. Ag28/Pt16, Ag22/Au6/Pd6 and Ag16/Au6/Pd6 multi-layers. Based on the enhanced diffusion, intermixing, alloying and the dewetting of various surface nanostructures such as voids, inter-connected, isolated irregular and round NPs were obtained. By the addition of new metal component, the dewetting degree was significantly altered, which gave rise to the distinct surface morphology at identical temperatures. Meanwhile, annealing at high temperature produced the well-spaced round alloy NPs due to the increased diffusion and extensive sublimation of Ag atoms. Furthermore, the optical characterization of the corresponding alloy NPs revealed the tunable LSPR bands depending upon the morphology, size and composition of NPs. In specific, the multi-metallic NPs exhibited dynamic MP and HO plasmon resonance bands at UV and VIS region, whose intensity was reduced with Ag sublimation and peak position was blue shifted with size reduction.

Acknowledgments

Financial support from the National Research Foundation of Korea (no. NRF-2019R1A2C4069438 and NRF-2018R1A6A1A03025242) and in part by the research grant of Kwangwoon University in 2019 is gratefully acknowledged. Also, the work reported in this paper was conducted during the sabbatical year of Kwangwoon University in 2019. Special appreciations to Ms So Hee Kim from the Korea Institute of Science and Technology (KIST) for the SEM-EDX characterizations.

ORCID iDs

J Lee https://orcid.org/0000-0002-8768-8586

References

[1] Morawiec S, Mendes M J, Priolo F and Crupi I 2018 Plasmonic nanostructures for light trapping in thin-film solar cells Mater. Sci. Semicond. Process. 92 10–18
[2] Yao Y C, Hwang J M, Yang Z P, Haung J Y, Lin C C, Shen W C and Tsai M T 2016 Enhanced external quantum efficiency in GaN-based vertical-type light-emitting diodes by localized surface plasmons Sci. Rep. 6 22659
[3] Wang J and Jia Z 2018 Metal nanoparticles/porous silicon microcavity enhanced surface plasmon resonance fluorescence for the detection of DNA Sensors 18 661
[4] Guo C F, Sun T, Cao F, Liu Q and Ren Z 2014 Metallic nanostructures for light trapping in energy-harvesting devices Light: Sci. Appl. 3 e161
[5] Lee K S and El-Sayed M A 2006 Gold and silver nanoparticles in sensing and imaging: sensitivity of plasmon response to size, shape, and metal composition J. Phys. Chem. B 110 19220–5
[6] Li X, Li G, Zhang W, Wang L and Zhang X 2014 Catalytic activity of shaped platinum nanoparticles for hydrogenation: a kinetic study Catal. Sci. Technol. 4 3290–7
[7] Hayaraja N, Prabu N, Lakshminarasimhan N, Murugan P and Jayakumar D 2013 Au–Pt graded nano-alloy formation and its manifestation in small organics oxidation reaction J. Mater. Chem. A 1 4046–56
[8] Venkatesan P and Santhanalakshmi J 2010 Designed synthesis of Au/Ag/Pd trimetallic nanoparticle-based catalysts for Sonogashira coupling reactions Langmuir 26 12225–9
[9] Song P, Xu H, Yan B, Wang J, Gao F, Zhang Y and Du Y 2018 Particle size effects of PtAg nanoparticles on the catalytic electrooxidation of liquid fuels Inorg. Chem. Frontiers 5 1174–9
[10] Wang F, Jiang Y, Lawes D J, Ball G E, Zhou C, Liu Z and Amal R 2015 Analysis of the promoted activity and molecular mechanism of hydrogen production over fine Au–Pt alloyed TiO2 photocatalysts ACS Catal. 5 3924–31
[11] Verma P, Kuwahara Y, Mori K and Yamashita H 2015 Synthesis and characterization of a Pd/Ag bimetallic nanocatalyst on SBA-15 mesoporous silica J. Mater. Chem. A 3 18889–97
[12] Verma P, Kuwahara Y, Mori K and Yamashita H 2016 Pd/Au and Pd/Au bimetallic nanocatalysts on mesoporous silica for plasmon-mediated enhanced catalytic activity under visible light irradiation J. Mater. Chem. A 4 10142–50
[13] Nguyen N T, Ozkan S, Tomanc S, Zhou X, Zboril R and Schmuki P 2018 Nanoporous AuPt and AuPtAg alloy co-catalysts formed by dewetting-dealloying on ordered TiO2 nanotube surface lead to significantly enhance photocatalytic H2 generation J. Mater. Chem. A 6 13599–606
[14] Mazumder V, Chi M, More K L and Sun S 2010 Synthesis and characterization of multimetallic Pd/Au and Pd/Au/FePt core/shell nanoparticles Angew. Chem. Int. Ed. 49 9368–72
[15] Louis C 2016 Chemical preparation of supported bimetallic catalysts, Gold-based bimetallic, a case study Catalysts 6 110
[16] Chen J, Wiley B, McLellan I, Xiong Y, Li Z Y and Xia Y 2005 Optical properties of Pd–Ag and Pt–Ag nanoboxes synthesized via galvanic replacement reactions Nano Lett. 5 2058–62
[17] Chen W, Yu R, Li L, Wang A, Peng Q and Li Y 2010 A seed-based diffusion route to monodisperse intermetallic CuAu nanocrystals Angew. Chem. Int. Ed. 49 2917–21
[18] Pandey P, Kunwar S, Sui M, Bastola S and Lee J 2018 Modulation of morphology and optical property of multi-metallic PdAuAg and PdAg alloy nanostructures Nanoscale Res. Lett. 13 151
[19] Sharma G, Kumar A, Sharma S, Naushad M, Dwivedi R P, ALothman Z A and Molla G T 2017 Novel development of nanoparticles to bimetallic nanoparticles and their composites: a review J. King Saud Univ.-Sci. 31 257–69
[20] Braidy N, Purdy G R and Bottom G A 2008 Equilibrium and stability of phase-separating Au–Pt nanoparticles Acta Mater. 56 5972–83
[21] Nugroho F A, Iandolo B, Wagner J B and Langhammer C 2016 Bottom-up nanofabrication of supported noble metal alloy nanoparticle arrays for plasmonics ACS Nano 10 2871–9
[22] Yang P, Zheng J, Xu Y, Zhang Q and Jiang L 2016 Colloidal synthesis and applications of plasmonic metal nanoparticles Adv. Mater. 28 10508–17
[23] Si S, Liang W, Sun Y, Huang J, Ma W, Liang Z, Bao Q and Jiang L 2016 Facile fabrication of high-density Sub-1-nm gaps from Au nanoparticle monolayers as reproducible SERS substrates Adv. Funct. Mater. 26 8137–45
[24] Sun J, Li Z, Sun Y, Zhong L, Huang J, Zhang J, Liang Z, Chen J and Jiang L 2018 Uniform and reproducible plasmon-enhanced fluorescence substrate based on PMMA-coated, large-area Au@Ag nanorod arrays Nano Res. 11 953–65
[25] Jiang L, Chen X, Lu N and Chi L 2014 Spatially confined assembly of nanoparticles Acc. Chem. Res. 47 3009–17
[26] Park E D (ed) 1998 Handbook of Optical Constants of Solids vol 3 (New York: Academic)
[27] Rakic D, Djuriuc A, Elazar J M and Majewski M L 1998 Optical properties of metallic films for vertical-cavity optoelectronic devices Appl. Opt. 37 5271–83
[28] Kang M, Ahn M-S, Lee Y and Jeong K-H 2017 Bioplasmic alloyed nanoidolands using dewetting of bilayer thin films ACS Appl. Mater. Interfaces 9 37154–9
[29] Yang G, Fu X J, Sun J-B and Zhou J 2013 Spectroscopic ellipsometry study on the optical dielectric properties of silver platinum alloy thin films J. Alloys Compd. 551 352–9
[30] Sui M, Li M Y, Kunwar S, Pandey P, Zhang Q and Lee J 2017 Effects of annealing temperature and duration on the morphological and optical evolution of self-assembled Pt nanostructures on c-plane sapphire PLoS One 12 e0177048
[31] Thompson C V 2012 Solid-state dewetting of thin films Annu. Rev. Mater. Res. 42 399–434
[32] Esterina R, Liu X M, Adeyeye A O, Ross C A and Choi W K 2015 Solid-state dewetting of magnetic binary multilayer thin films J. Appl. Phys. 118 144902
[33] Herz A, Franz A, Theska F, Hentschel M, Kups T, Wang D and Schaaf P 2016 Solid-state dewetting of single- and bilayer Au–W thin films: unravelling the role of individual layer thickness, stacking sequence and oxidation on morphology evolution AIP Adv. 6 035109
[34] Kunwar S, Pandey P, Sui M, Bastola S and Lee J 2017 Evolution of ternary AuAgPd nanoparticles by the control of temperature, thickness, and tri-layer Metals 7 472
[35] Kwon J Y, Yoon T S, Kim K B and Min S H 2003 Comparison of the agglomeration behavior of Au and Cu films sputter deposited on silicon dioxide J. Appl. Phys. 93 3270–8
[36] Herz A, Wang D, Kups T and Schaaf P 2014 Solid-state dewetting of Au/Ni bilayers: the effect of alloying on morphology evolution J. Appl. Phys. 116 044307
[37] Hansen M 1958 U. K. Anderko: Constitution of Binary Alloys (New York: McGraw-Hill) vol 2, p 989
[38] Sui M, Pandey P, Kunwar S, Li M Y, Zhang Q and Lee J 2016 Evolution of self-assembled Ag nanostructures on c-plane sapphire by the systematic control of annealing temperature Superlattices Microstruct. 100 1128–42
[39] Lian R, Yu H, He L, Zhang L, Zhou Y, Bu X and Sun L 2016 Sublimation of Ag nanocrystals and their wetting behaviors with graphene and carbon nanotubes Carbon 101 368–76
[40] Yang T and Crozier K B 2008 Dispersion and extinction of surface plasmons in an array of gold nanoparticle chains: influence of the air/glass interface Opt. Express 16 8570–80
[41] Siabi-Garjana A and Savaloni H 2013 Extinction spectra and electric field enhancement of silver chiral nano-flower shaped nanoparticle; comparison of discrete dipole approximation results with experimental results Euro. Phys. J. B 86 257
[42] Wang Z and Rothberg I J 2006 Silver nanoparticle coverage dependence of surface-enhanced Raman scattering Appl. Phys. B 84 289–93
[43] Langhammer C, Yuan Z, Zoric I and Kasemo M 2006 Plasmonic properties of supported Pt and Pd nanostructures Nano Lett. 6 833–8
[44] Paris A, Vaccari A, Lesina A C, Serra E and Calliari L 2012 Plasmonic scattering by metal nanoparticles for solar cells Plasmonics 7 525–34
[45] Langhammer C, Kasemo B and Zoric I 2007 Absorption and scattering of light by Pt, Pd, Ag, and Au nanodisks: absolute cross sections and branching ratios J. Chem. Phys. 126 194702
[46] Vitous L, Ruban A V, Skriver H L and Kollar J 1998 The surface energy of metals Surf. Sci. 411 186–202
[47] Pandey P, Kunwar S, Sui M, Bastola S and Lee J 2018 Role of annealing temperature, time, and composition on the fabrication of AuxPd1–x nanostructures on c-plane sapphire by the solid-state dewetting of bimetallic thin films IEEE Trans. Nanotechnol. 17 325–31