Improved LSPR Properties of Ag–Pt and Pt Nanoparticles: A Systematic Study on Various Configurations and Compositions of NPs via the Solid-State Dewetting of Ag–Pt Bilayers

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Abstract: The localized surface plasmon resonance (LSPR) of noble metal nanoparticles (NPs) has become an important research topic in various fields and can be systematically tuned to obtain the desired device performance through the appropriate structural and elemental modifications. In this research, the improved LSPR properties of Pt NPs and diverse configurations and compositions of Ag–Pt bimetallic alloy NPs were demonstrated on sapphire (0001) via the solid-state dewetting (SSD) of Ag–Pt bilayers. A strong and dynamic LSPR response in the ultraviolet (UV) and visible (VIS) regions was demonstrated depending on the elemental composition and surface morphology of the NPs, which is discussed along with finite difference time domain (FDTD) simulations. In comparison, the Ag–Pt NPs exhibited stronger LSPR excitation, whereas the Pt NPs showed a relatively weaker and broader response. Meanwhile, the Pt NPs fabricated in this study still demonstrated a much-enhanced LSPR response compared to previous studies on the solid-state dewetting of pure Pt films due to improvements in configuration, uniformity, and interparticle gaps. Various surface morphologies of NPs, such as connected nanoclusters, elongated NPs, and isolated spherical NPs, were obtained on the basis of alloying, diffusion, Rayleigh instability, and a surface minimization mechanism, which were different from those of pure Ag and Pt NPs in similar growth conditions. Particularly, one-step annealing of an Ag–Pt bilayer yielded Ag–Pt alloy NPs below 600 °C, which subsequently transformed into pure Pt NPs above 650 °C, in which the high diffusivity and high vapor pressure of Ag atoms significantly facilitated the overall growth process of the NPs.

Keywords: plasmonics; solid-state dewetting; alloy nanoparticles; Ag–Pt NPs; FDTD

1. Introduction

Metallic nanoparticles (NPs) can exhibit various unique optical, electrical, chemical, electronic, and catalytic properties resulting from their strong surface plasmon resonance, high carrier concentration, photon–electron conversion, and high surface-to-volume ratio [1–3]. Thus, these metallic NPs have been extensively adapted in a wide range of applications, such as in solar cells, catalysis, sensors, energy harvesting, and biomedical devices [4–8]. For example, the energy conversion efficiency in energy-harvesting devices can be significantly improved through enhanced light trapping by plasmonic NPs due to strong localized surface plasmon resonance (LSPR) [7]. At the same time, the integration of multiple elements in an NP, namely multimetallic NPs, can be an effective approach in realizing improved performance in related applications due to the synergetic multifunctionality, elemental heterogeneity, and dynamic tunability of NPs [9–13]. Alloy nanocrystals exhibit superior
Electrocatalyst activities in methanol oxidation reactions along with strong durability compared to pure Pt catalysts [14].

Generally, there have been several methods practiced for the preparation of bimetallic alloy NPs, such as chemical coreduction [15], seeded growth [16], and laser-induced ablation [17]. While these methods have been successfully demonstrated, the NPs produced are in the form of colloidal solutions, and many plasmonic and catalytic applications require the fabrication of alloy NP arrays that stably adhere to a substrate [18]. Among the various noble metallic elements, Ag and Pt are of particular interest due to their strong LSPR and catalytic response (respectively). For instance, the Ag–Pt alloy material is one of the most promising candidates for cathode materials in fuel cell applications due to enhanced photocatalytic activity. The integration of Ag and Pt into a single NP matrix can be an important research topic in realizing the improved plasmonic activity of Ag NPs as well as the chemical durability of Pt NPs, and this has not been reported in detail using the solid-state dewetting (SSD) approach. At the same time, the SSD of pure Pt films has yielded wide coverage and poorly developed NPs in the usual growth conditions due to low diffusivity, while Ag atoms possess high diffusivity and thus have produced well-developed isolated Ag NPs. Therefore, synergistic diffusion enhancement between Ag and Pt atoms could enhance overall dewetting to produce well-structured alloy NPs, which could have importance not only in fundamental research but also in practical applications.

In this work, the fabrication of various configurations and arrangements of Ag–Pt and Pt NPs are demonstrated through the SSD of Ag–Pt bilayer films on sapphire (0001). Due to the variation in elemental composition, the bimetallic alloy NPs provided an additional flexibility to tune the LSPR properties. In general, the nanostructures gradually evolved from connected, elongated, and isolated to round NPs due to thermally activated atomic diffusion, intermixing, nucleation, and energy minimization along with annealing temperature modification, as illustrated in Figure 1. Various configurations of Ag–Pt alloy nanostructures were fabricated below 600 °C, while monometallic Pt NPs resulted above 650 °C due to preferential Ag atom sublimation. Morphology and elemental modifications were directly captured by atomic force microscope (AFM) and energy-dispersive X-ray spectroscopy (EDS) characterizations, which were correspondingly reflected in the LSPR properties, showing dynamic absorption bands in the ultraviolet (UV) and visible (VIS) regions.

2. Materials and Methods

In this work, the morphological and optical properties of Ag–Pt and Pt nanostructures were investigated on transparent c-plane sapphire (0001). Initially, double-side polished 430-μm-thick sapphire (0001) wafers with an off-axis of ±0.1° (iNexus Inc., Seoul, Korea) were diced into 6 × 6 mm² square pieces. Then, the sapphire substrates were degassed in a pulsed laser deposition (PLD) chamber (DaDa TG, Dalseong-gu, Daegu-si, Korea) at 600 °C for 30 min under 1 × 10⁻⁴ Torr in order to remove surface contaminants such as vapors, oxides, and particulates. The surface morphology of degassed sapphire was found to be smoother, with a surface roughness of ~0.12 nm, as shown in Appendix A Figure A1.

Three series of Ag–Pt bilayer films were prepared, i.e., Ag₇₀ nm/Pt₁₅ nm, Ag₂₈ nm/Pt₀.₆ nm, and Ag₁₅ nm/Pt₇.₅ nm. The deposition of Ag–Pt bilayer films was carried out in an ion-coater chamber through sputtering. Both metal layers were deposited at a constant growth rate of 0.05 nm/s with a 3-mA ionization current under a vacuum of 1 × 10⁻¹ Torr. For the growth of nanostructures, the as-deposited samples were annealed at each target annealing temperature (Tₐ) between 500 and 900 °C in a PLD chamber under 1 × 10⁻⁴ Torr. Each sample was allocated with 120 s of dwelling duration after reaching the target temperature for the matured growth of nanostructures.

The fabricated Ag–Pt and Pt nanostructures were imaged by an atomic force microscope (AFM, Park Systems Corp., Suwon, Korea) in an ambient environment and processed with XEI software (Park Systems Corp., Suwon, Korea) for further analyses. An additional morphological analysis was performed with a scanning electron microscope (SEM, COXEM Co. Ltd, Yuseong-gu, Daejeon, Korea and Regulus 8230, HITACHI, Matsumoto-shi, Nagano, Japan). An elemental analysis of the Ag–Pt
Metals 2019, 9, 1011

and Pt nanostructures was performed with an energy-dispersive X-ray spectrometers (EDS, Thermo Fisher Scientific, Waltham, MA, USA and Ultimax, Oxford Instruments, Abingdon, UK). In addition, the LSPR properties of as-fabricated NPs were investigated using reflectance and transmittance spectra from an NOST system (Nostoptiks Co. Ltd, Seongnam-si, Gyeonggi-do, Korea) equipped with an ANDOR spectrograph, a CCD detector, combined halogen–deuterium light sources, etc. The extinction spectra were extracted by using the relation $R\% + T\% + E\% = 100\%$.

In addition, a finite difference time domain (FDTD) simulation on typical Ag–Pt and Pt NPs was performed (Lumerical Solutions, Vancouver, BC, Canada). Typical 3D AFM images were imported into the object space to incorporate the real surface feature of NPs on sapphire. A total field-scattered field (TFSF) wave source 250 to 1000 nm in wavelength was used to excite the NPs on sapphire from the $z$ direction. In all directions, a perfectly matched layer (PML) boundary condition was applied. The gap between the PML boundary and the nanostructures was about 500 nm in all directions to avoid interference. For the simulation, an auto-shut-off level of $10^{-6}$ and a 3D mesh grid of 0.5 to 5 nm were used. The refractive indices of sapphire and Pt were based on Palik’s model, while those of Ag were based on Rakic’s model [19,20]. The dielectric constant of the Ag–Pt alloy was averaged from the dielectric constant of pure Ag and Pt based on the atomic percentage (at %) fraction [21,22].

3. Results and Discussion

Figure 1 shows the fabrication steps of self-assembled Ag–Pt and Pt nanostructures on sapphire (0001) through the annealing of Ag–Pt bilayers. The formation of isolated NPs from the Ag–Pt bilayer films at successive annealings below the melting point of Ag and Pt can be discussed based on solid state dewetting (SSD), as described in Figure 1a–d. In the case of the monometallic films, the dewetting process was mainly governed by the temperature-driven diffusion of atoms, i.e., the higher diffusivity yielded a higher dewetting rate and thus well-developed surface NPs. In previous studies, due to the low diffusivity of Pt atoms, interconnected and irregular Pt NPs were fabricated with pure Pt thin films on sapphire even at an annealing temperature ($T_a$) above 800 °C [23]. Meanwhile, well-developed and isolated Ag NPs were demonstrated under similar growth conditions with Ag films [24]. The SSD of the bilayers involved additional mechanisms such as interdiffusion, alloying, and diffusion in the alloy phase, as shown in Figure 1b,c, and thus the dewetting process and resulting nanostructures could be drastically different from the monometallic films [25,26]. In general, due to the broad miscibility gap between Ag and Pt and the large difference in the melting point of Ag (961.8 °C) and Pt (1768 °C), Ag–Pt alloy formation in the bulk phase is challenging [26]. However, with nanoscale Ag–Pt bilayers, the intermixing of Ag and Pt atoms could sufficiently occur at $T_a$, way below the melting point, due to the atomic interdiffusion at the Ag–Pt interface, as illustrated in Figure 1b. This could lead to the alloying of Ag–Pt atoms, and thus the global diffusion of the atoms could be much increased. Eventually, the SSD could begin through the nucleation of voids and the accumulation of diffusing atoms, which resulted in the evolution of Ag–Pt alloy NPs at an intermediate $T_a$, as shown in Figure 1c. This process could be driven by the surface and interface energy minimization between film and substrate. Meanwhile, with further increased $T_a$, the evolution of Ag–Pt alloy NPs could be attributed to the sublimation of Ag atoms because of the high vapor pressure of Ag at temperatures above 500 °C. This eventually could result in the formation of pure Pt NPs, as illustrated in Figure 1d. These pure Pt NPs (obtained at a $T_a$ above 650 °C) could be expected to differ largely in terms of structure and LSPR response from pure Pt dewetting, as presented in the typical extinction spectra and local e-field of NPs in Figure 1e–g.
Figure 1. Schematic illustration of Ag–Pt and Pt nanoparticle (NP) fabrication mechanisms on sapphire (0001) through the annealing of Ag–Pt bilayers. (a) Ag–Pt bilayer. (b) Atomic interdiffusion, void nucleation, and agglomeration at a low annealing temperature. (c) Formation of Ag–Pt alloy NPs along with Ag sublimation. (c-1–c-3) Typical Ag–Pt alloy nanoclusters and elemental maps. (d) Evolution of Pt NPs. (d-1) Atomic force microscope (AFM) image and line profile of typical Pt NP. (e) Extinction spectra for typical Ag–Pt and Pt NPs. (f,g) Local e-field of typical Ag–Pt and Pt NPs.

Figures 2 and 3 show the detailed morphological and elemental evolution of various Ag–Pt and Pt NPs in Ag\text{70 nm}/Pt\text{15 nm} bilayers with SEM, AFM, and EDS characterizations. The nanoscale voids and granular structures were formed as an initial stage of dewetting at 500 °C, as displayed in Figures 2a and 3a. These pinholes and voids could preferentially form at the low-energy sites and grow larger due to adatom diffusion as well as the coalescence of atomic vacancies. The void growth rate \(v_h\) depends upon the atomic diffusivity and thickness of the film according to the relation \(v_h = \frac{2D_\alpha \rho\gamma_{fe}}{kT h}\), where \(D_\alpha\), \(\rho\), \(\gamma\), \(\gamma_{fe}\), and \(h\) are diffusivity, the surface density of the atoms, atomic volume, surface energy,
and film thickness, respectively [27]. Thus, along with the increased $T_a$ between 550 and 600 °C at a constant film thickness, the $D_s$ increased correspondingly, causing vacancy coalescence. This resulted in the formation of larger voids more than 1 µm in width and network-like Ag–Pt nanostructures 200 nm in height, as displayed in Figure 2b,c and Figure 3b,c.

The surface evolution was also reflected in terms of a Fourier-filter transform (FFT) pattern, root mean squared (RMS) roughness ($R_q$), and the surface area ratio (SAR) as a function of $T_a$. The FFT patterns were gradually enlarged due to height fluctuation along with the evolution of voids. Similarly, increments of $R_q$ and SAR with temperature were observed, as shown in Figure 3g,h, which indicates an increase in the average surface height and area due to the formation of 3D Ag–Pt nanoclusters on the layered films. Meanwhile, along with the increased dewetting rate, the evolution of Ag–Pt nanoclusters could be affected by the sublimation of Ag atoms due to their high vapor pressure, as mentioned. To confirm the sublimation of Ag atoms in the alloy nanostructures, an elemental analysis on each sample was performed using an EDS measurement, as shown in Figure 3i. The EDS counts of Pt Mα1 appeared to be similar, while the Ag Mα1 counts were sharply reduced between 500 and 600 °C, indicating the sublimation of Ag atoms. The sublimation rate of Ag also depended on the temperature and vapor pressure, as given by the relation $R_s = (3.513 \times 10^{22}) \left(\frac{T}{M_{Ag}}\right)^{-1/2} \times P_{eq}$, where $R_s$ is the rate of sublimation, $T$ is temperature, $M_{Ag}$ is the molecular weight of silver, and $P_{eq}$ is the equilibrium vapor pressure of Ag [28,29]. In the vapor pressure versus temperature curve, $P_{eq}$ exponentially increased with temperature. Thus, the Ag atoms could abruptly sublimate with the increased $T_a$, and pure Pt could be formed.

![Figure 2](image_url)

**Figure 2.** Evolution of the Ag–Pt and Pt NPs on sapphire (0001) through the annealing of Ag$_{70}$ nm/Pt$_{15}$ nm bilayers between 500 and 900 °C for 450 s. (a–f) SEM images and (a-1–f-1) corresponding AFM top-views ($5 \times 5 \mu m^2$). Insets show the Fourier-filter transform (FFT) patterns of the AFM images.
Figure 3. Evolution of the Ag–Pt and Pt NPs on sapphire (0001) through the annealing of Ag70 nm/Pt15 nm bilayers between 500 and 900 °C for 450 s. (a–f) AFM side-views (1.5 x 1.5 µm²). (g,h) Plots of root mean squared (RMS) roughness (Rq) and surface area ratio (SAR). (i) Summary plot of energy-dispersive X-ray spectroscope (EDS) count of the Pt Mα1 and Ag Lα1 peaks. The Ag Lα1 count was zero above 650 °C. (j–l) SEM image and Pt and Ag maps of Ag–Pt nanoclusters fabricated at 600 °C. (m) EDS spectra line profile acquired from the arrow in (j). (n,o) EDS spectra acquired from the boxed regions in (j).

Furthermore, elemental distribution and alloy formation in the Ag–Pt nanoclusters were investigated in detail with the sample at 600 °C, as shown in Figure 3j–o. The SEM image and Pt and Ag phase maps in Figure 3j–l matched perfectly, indicating the homogeneous mixture of Ag and Pt in the nanostructures. This can also be seen in the EDS line profile extracted from an Ag–Pt nanocluster in Figure 3m. In addition, the EDS spectra of the nanostructure region clearly show the Pt and Ag peaks, while the void region has no Ag and Pt peaks, as shown in Figure 3n,o, respectively. As the Ag atoms were completely sublimated above 600 °C, the surface morphology was drastically transformed such that patterned and partially segmented Pt NPs were obtained at 650 °C, as shown in Figures 2d and 3d. The fragmentation of isolated patterned Pt NPs from the connected nanocluster could have been due to Rayleigh-like instability [27]. When Ta was increased between 750 and 900 °C,
the patterned Pt NPs were further isolated and became more uniform, as displayed in Figure 2e,f, which demonstrated a unique morphological evolution compared to pure Pt dewetting [23,24]. This could have been correlated with the combinational effects of Ag–Pt alloying, the enhanced surface diffusion of atoms, the sublimation of Ag, and surface energy minimization [30]. Since the average vertical size and surface area of Pt NPs were significantly decreased compared to the Ag–Pt nanoclusters, $R_q$ and the SAR were also sharply decreased. At the higher $T_A$, $R_q$ and the SAR were found to be similar or slightly increased, likely due to the mild growth of Pt NPs.

Figure 4 shows the LSPR properties of the Ag–Pt and Pt nanostructures fabricated with Ag$_{70}$ nm/Pt$_{15}$ nm in terms of extinction, reflectance, and transmittance spectra. In addition, the local e-field enhancement of a typical Ag–Pt and Pt NP is simulated in Figure 5. The material constants of alloy nanostructures were determined by averaging the pure Ag and Pt on the basis of the atomic percentage (at %) of Ag and Pt, as discussed [21,22]. The simulated extinction spectra are provided in Figure A4. In general, depending upon the structural configuration and elemental composition of the nanostructures, the optical spectra exhibited distinct wavelength-dependent behaviors. First of all, the extinction spectra in Figure 4a demonstrate two distinctive LSPR bands, including the intense absorption peaks in the UV and VIS region with the Ag–Pt alloy nanoclusters at a temperature below 650 °C, whereas a relatively weaker and broader absorption peak was observed with the Pt NPs above 650 °C. This could have been caused by the desorption of Ag atoms as well as the size reduction of nanoclusters with temperature [31]. Since the NPs in this set were larger than 400 nm in width and had a wide size distribution, the dipolar, quadrupolar, and other resonance modes could overlap and give rise to a superimposed multipolar resonance mode in the VIS region and a higher-order resonance mode in the UV region [32]. Thus, the development of an extinction peak in the VIS region at around 500 nm in Figure 4a could be related to a multipolar resonance mode, and that in the UV region at around 300 nm could be assigned to a higher-order plasmon resonance mode. In a simulation of a typical Ag–Pt alloy nanocluster, as shown in Figures 5a–c and A4, multiple extinction maxima appeared in the visible region at around 470, 580, and 750 nm due to the excitation of various plasmonic modes, as discussed. Thus, it can be speculated that Ag–Pt nanoclusters with wide coverage and size distributions could have resulted in the formation of a stronger superimposed LSPR band in the UV-VIS region. In the e-field profiles (shown in Figure 5b,c), the e-field was stronger at the boundary (or surface) of the NPs. An e-field vector related to the multipolar resonance mode showed multiple directions, as shown in Figure 5b-1,c-1.

In the case of isolated Pt NPs between 650 and 900 °C, while much reduced absorption bands were observed, the VIS absorption band was slightly increased at a high $T_A$, with slightly improved uniformity of Pt NPs, as displayed in Figure 4a-2. The e-field was very confined at the boundary, and the number of extinction maxima in the visible region were decreased in the case of Pt NPs, as observed in Figure 5e,f and Figure A4. On the other hand, the extinction maxima were significantly blue-shifted at around 315 and 500 nm because of the smaller size of the Pt NPs. Similarly, the e-field vectors were also altered, and the number of vector directions was reduced, which could have been correlated with the excitation of less-plasmonic modes with the reduced size and improved uniformity of Pt NPs. Furthermore, the corresponding reflectance spectra are presented in Figure 4b, and they exhibited a narrow absorption dip in the UV region and a wide absorption dip in the VIS region corresponding to the higher order and multipolar resonance modes of nanostructures, as discussed. For the Ag–Pt alloy nanostructures, the absorption dips were generally strong but were gradually reduced with the desorption of Ag at increased $T_A$, as shown in Figure 4b-1. For the Pt NPs at a high $T_A$, the absorption was much reduced and broadened, as shown in Figure 4b-2. The broadening of the absorption dip in the VIS region (with a low Ag content and Pt NPs) is shown in Figure 4b-3.
Figure 4. Optical properties of the Ag–Pt and Pt nanoclusters fabricated with the Ag_{70 nm}/Pt_{15 nm} bilayers. (a–a-3) Extinction, normalized extinction, and enlarged extinction spectra. (b–b-3) Reflectance, normalized reflectance, and enlarged absorption dip. (c–c-2) Transmittance and normalized transmittance spectra. (d) Summary plots of average reflectance and transmittance.
Figure 5. Finite difference time domain (FDTD) simulations of the Ag–Pt and Pt NPs fabricated at 600 and 900 °C with the Ag$_{70}$ nm/Pt$_{15}$ nm bilayers. (a,d) AFM images with corresponding line profiles of Ag–Pt and Pt NPs. (a-1–d-1) Cross-sectional line profiles. (b,c,e,f) Electric-field profiles in x–y plane. (b-1,c-1,e-1,f-1) E-field vector plots at corresponding wavelengths.

In the transmittance spectra, a sharp distinction between the Ag–Pt alloy and the Pt NPs was observed, as shown in Figure 4c. In particular, lower transmittance was observed for the lower Ta samples due to the wide surface coverage of the Ag–Pt nanostructures. The normalized transmittance spectra of the Ag–Pt alloy nanostructures in Figure 4c-1 demonstrated low absorption in the VIS region, likely due to high forward scattering [33]. With increased Ta, the absorption dip became smoother (along with the formation of Pt NPs), likely due to the gradual reduction of forward scattering as the size of the NPs was reduced compared to the Ag–Pt NPs. For the Ag–Pt nanostructures, the average reflectance was generally high, while the transmittance was low, as presented in Figure 4d, due to high surface coverage. The opposite was observed for the Pt NPs due to much-reduced coverage. In short, the Ag–Pt NPs with an Ag component showed much-improved plasmonic properties [23,24]. While the Pt NPs in this study showed a much-reduced extinction response compared to the Ag–Pt...
NPs, these reflectance spectra still demonstrated enhanced plasmonic peaks in the UV and VIS regions compared to the pure Pt NPs in the previous study [24].

Figure 6 shows the fabrication of tiny Ag–Pt and Pt NPs on sapphire (0001) with the Ag$_{2.8}$ nm/Pt$_{0.6}$ nm bilayers at 550 and 800 °C. The detailed evolution of NPs at specific $T_a$ is presented in Figure A5, along with AFM top-views, side-views, and cross-sectional line profiles. Generally, the dewetting of thin film inversely depends upon the initial film thickness, i.e., the thinner the film, the higher the dewetting rate [34]. In this set, due to the much thinner thickness of the Ag–Pt bilayer with a high percentage of Ag, the much-enhanced diffusion, alloying, and nucleation of isolated NPs could be achieved at a low $T_a$. Thus, the NPs obtained were very small and dense compared to the previous set. For instance, densely packed Ag–Pt alloy NPs 8 nm in height and 40 nm in diameter were formed at 550 °C, as shown by the AFM top-views and color-coded side-views in Figure 6a,a-1. The corresponding cross-sectional line profile revealed the height of the Ag–Pt NPs, which was nearly 12 times smaller than the previous set in identical conditions. Furthermore, these NPs attained an isolated and round shape even at low $T_a$ due to enhanced diffusion through the alloying of atoms [34]. As the $T_a$ increased, the size of the NPs was reduced, as shown in Figure 6b, due to the rapid sublimation of the Ag atom. At a $T_a$ above 600 °C, the Ag atoms were fully desorbed from the NP matrix, and as a result, pure Pt NPs were formed. The average size of the Pt NPs was less than 5 nm in height and 25 nm in diameter, as clearly shown by the cross-sectional line profiles in Figure 6b-2. Additionally, the overall growth in the NP size is expressed in terms of $R_q$ and the SAR, as displayed in Figure 6c,d. As $T_a$ increased between 500 and 800 °C, $R_q$ and the SAR gradually decreased due to the reduction in height and surface area of the NPs.

The corresponding optical properties of small and dense Ag–Pt and Pt NPs fabricated with the Ag$_{2.8}$ nm/Pt$_{0.6}$ nm bilayers are presented in Figure 6e–g. Based on the distinct size and elemental composition of the NPs, the extinction, reflectance, and transmittance spectra showed distinctive responses from the previous set. In general, the extinction spectra in Figure 6e,e-1 exhibited a comparatively stronger absorption peak in the VIS region (~490 nm) and a weaker peak in the UV region (~310 nm). As the NP size was much smaller in this set (<12 nm in height and <50 nm in diameter), the corresponding two extinction peaks could be assigned to the quadrupolar resonance mode at ~310 nm and the dipolar resonance mode at ~490 nm [34]. The localized e-field distribution on a typical Ag–Pt NP was simulated, as shown in Figure 7. First, the simulation was performed with an imported typical AFM image using the model explained in the experimental section. As shown in Figure 7c,d, a dipolar plasmonic mode was observed, with extinction maxima at ~420 nm. The simulated extinction peak was blue-shifted compared to the experimental one, which could have been due to the disparity in size between the AFM image and real NPs. In addition, an ideal semi-ellipsoid 40 nm in diameter and 8 nm in height corresponding to the average size and dimension of the Ag–Pt NPs was simulated using a periodic boundary condition in the $x$, $y$ directions with 80 nm of periodicity, as shown in Figure 7e,f. A dipolar resonance mode was observed at ~520 nm, which showed a strong e-field confinement on the surface of the NPs, as shown in Figure 7f,g. Furthermore, a quadrupolar shoulder was observed in the UV region, as seen in Figure 7e. The simulated and experimental extinction spectra generally agreed well, although the resonance peak positions were somewhat deviated, likely due to the difference in real and simulated NPs.
Figure 6. Small and highly dense Ag–Pt and Pt NPs on sapphire (0001) with the Ag$_{2.8}$ nm/Pt$_{0.6}$ nm bilayers at 550 and 800 °C. (a,b) AFM top-views (700 × 700 nm$^2$). Insets show the magnified AFM top-views of 100 × 100 nm$^2$. (a-1–b-1) AFM side-views. (a-2–b-2) Cross-sectional line profiles. (c,d) Summary plots of R$_q$ and SAR. (e–e-2) Extinction, normalized extinction, and enlarged visible region peak. (f) Reflectance spectra. (g,g-1) Transmittance and normalized transmittance spectra.
Likewise, the absorption dip gradually widened with the formation of smaller Pt NPs at gradually reduced with a higher $Ta$ corresponding to quadrupolar and dipolar resonance modes, as discussed [33]. The absorption was narrow absorption dip in the UV region (~310 nm) and a wide absorption dip in the VIS region (~490 nm) backward scattering with small NPs [31]. The corresponding transmittance spectra in Figure 6g reveal a instead of the shoulder; however, a shoulder was observed in the UV-VIS region due to enhanced the Pt NPs are presented in Figure 6f. Generally, an absorption dip could be expected in the VIS region shorter wavelengths than the large NPs in the previous set due to much smaller sizes and improved uniformity [32]. Furthermore, the dipolar resonance peak showed a gradual broadening at higher $Ta$ [34]. Specifically, the annealing of the nanoclusters started to fragment, likely due to Rayleigh-like instability, as shown in $Ta[34]$. When comparing them to previous sets, these voids were much smaller and denser due to the presence of Ag content and the relatively larger size of the NPs, as clearly shown by the strong dipolar resonance peaks. As the Ag atoms were gradually sublimated, relatively smaller Pt NPs were formed, and the intensity of the dipolar resonance peak was gradually reduced between 600 and 800 °C. Consequently, the evolution of the irregular voids in order to minimize the interface energy, as discussed [27,28].

In comparison to the previous set, the overall absorption was largely reduced in this set due to the much smaller size of the NPs with a lower Ag content. The extinction spectra were normalized in order to show the morphology and composition-dependent plasmonic responses in Figure 6e-1. Specifically, with Ag–Pt alloy NPs at 500 and 550 °C, the absorption peaks were relatively stronger due to the presence of Ag content and the relatively larger size of the NPs, as clearly shown by the strong dipolar resonance peaks. As the Ag atoms were gradually sublimated, relatively smaller Pt NPs were formed, and the intensity of the dipolar resonance peak was gradually reduced between 600 and 800 °C. Furthermore, the dipolar resonance peak showed a gradual broadening at higher $Ta$, as shown in Figure 6e-2 with the NP evolution. These dipolar resonance peaks were significantly narrower and had shorter wavelengths than the large NPs in the previous set due to much smaller sizes and improved uniformity [32]. Furthermore, the corresponding reflectance spectra of the small-sized Ag–Pt alloy and the Pt NPs are presented in Figure 6f. Generally, an absorption dip could be expected in the VIS region instead of the shoulder; however, a shoulder was observed in the UV-VIS region due to enhanced backward scattering with small NPs [31]. The corresponding transmittance spectra in Figure 6g reveal a narrow absorption dip in the UV region (~310 nm) and a wide absorption dip in the VIS region (~490 nm) corresponding to quadrupolar and dipolar resonance modes, as discussed [33]. The absorption was gradually reduced with a higher $Ta$ along with decreased NP size and Ag sublimation, as shown in Figure 6g-1. Likewise, the absorption dip gradually widened with the formation of smaller Pt NPs at

**Figure 7.** Finite difference time domain (FDTD) simulations of the small-sized Ag–Pt NPs fabricated with the Ag$_{2.8}$ nm/Pt$_{0.6}$ nm bilayers at 550 °C and ideal Ag–Pt NPs. (a) AFM images. (b) Cross-sectional line profile. (c,d) Simulated e-field profile and extinction spectra based on the imported AFM image. (e–g) Simulated extinction and e-field profiles of an ideal semi-ellipsoid Ag–Pt NP 40 nm in diameter and 8 nm in height, which is similar to the average size of the Ag–Pt NPs.

In comparison to the previous set, the overall absorption was largely reduced in this set due to the much smaller size of the NPs with a lower Ag content. The extinction spectra were normalized in order to show the morphology and composition-dependent plasmonic responses in Figure 6e-1. Specifically, with Ag–Pt alloy NPs at 500 and 550 °C, the absorption peaks were relatively stronger due to the presence of Ag content and the relatively larger size of the NPs, as clearly shown by the strong dipolar resonance peaks. As the Ag atoms were gradually sublimated, relatively smaller Pt NPs were formed, and the intensity of the dipolar resonance peak was gradually reduced between 600 and 800 °C. Furthermore, the dipolar resonance peak showed a gradual broadening at higher $Ta$, as shown in Figure 6e-2 with the NP evolution. These dipolar resonance peaks were significantly narrower and had shorter wavelengths than the large NPs in the previous set due to much smaller sizes and improved uniformity [32]. Furthermore, the corresponding reflectance spectra of the small-sized Ag–Pt alloy and the Pt NPs are presented in Figure 6f. Generally, an absorption dip could be expected in the VIS region instead of the shoulder; however, a shoulder was observed in the UV-VIS region due to enhanced backward scattering with small NPs [31]. The corresponding transmittance spectra in Figure 6g reveal a narrow absorption dip in the UV region (~310 nm) and a wide absorption dip in the VIS region (~490 nm) corresponding to quadrupolar and dipolar resonance modes, as discussed [33]. The absorption was gradually reduced with a higher $Ta$ along with decreased NP size and Ag sublimation, as shown in Figure 6g-1. Likewise, the absorption dip gradually widened with the formation of smaller Pt NPs at
increased $T_a$. In contrast to the previous set, this set revealed much narrower absorption dips in the VIS region due to the formation of much smaller and uniform NPs [32].

Figure 8 shows the gradual evolution of medium-sized Ag–Pt and Pt NPs from the Ag$_{15}$nm/Pt$_{7.5}$nm bilayers on sapphire (0001) through annealing between 500 and 900 °C for 120 s. This set of samples was prepared to realize medium-sized NPs under identical growth conditions. In general, the nanostructures were gradually evolved from interconnected and irregular to well-isolated semispherical configurations along with increased $T_a$. When comparing them to previous sets, these NPs were at the intermediate stage in size and density, as final size and configuration directly depended on the initial bilayer thickness, as discussed. In fact, the total deposition thickness as well as individual thickness of the bilayer was largely reduced compared to the first set. Therefore, the dewetting could occur much faster and at a relatively lower $T_a$ [34]. Specifically, the annealing of the Ag$_{15}$nm/Pt$_{7.5}$ bilayer at 500 °C developed numerous voids and connected nanostructures, as shown in Figure 8a,a-1. Compared to the first set at the same $T_a$, the voids were much smaller and denser due to the rapid nucleation of the thinner Ag–Pt bilayer. The voids were ~22 nm in depth and 70 nm in width, as clearly seen in the line profile in Figure 8a-2. Consequently, the evolution of the irregular Ag–Pt nanocluster was observed at 600 °C, which could be correlated with the coalescent growth of voids in order to minimize the interface energy, as discussed [27,28].

Meanwhile, the large nanoclusters started to fragment, likely due to Rayleigh-like instability, and the corresponding line profile showed increased average vertical height of the nanostructures, while the lateral width was sharply decreased. The FFT power spectra were gradually reduced in size, as presented in the insets of the AFM top-views, which could be correlated with decreased height distribution along with the evolution of Ag–Pt nanoclusters. In addition, $R_q$ and the SAR were sharply increased between 500 and 600 °C due to the increased height of the nanostructures and surface area exerted by the nanostructures, as shown in Figure 8g. Similarly to the previous sets, well-developed pure Pt NPs were obtained above 650 °C due to Ag sublimation, as shown in Figure 8d–f. The corresponding EDS counts and spectra are shown in Figure 8h,i, which exhibit nearly consistent Pt peak counts, indicating no desorption of Pt atoms regardless of the variant surface morphology with increased $T_a$. However, in the case of Ag peaks, the counts were sharply decreased between 500 and 600 °C and became equal to the background at higher $T_a$, as shown in Figure 8h. In addition, a detailed elemental analysis is presented in Figure 9. For a typical nanocluster fabricated at 550 °C, the SEM image matched well with the Ag and Pt phase maps, as shown in Figure 9a–d. Similarly, the EDS line profile through the nanoclusters revealed the similar intensity of Ag Kα1 and Pt Mα1. From the results, it was clear that the Ag and Pt atoms were well intermixed in the nanoclusters during the dewetting process.

Along with Ag sublimation, the large nanoclusters were further fragmented, resulting in smaller NPs at 650 °C. At this stage, the lateral size of nanostructures was extensively decreased, whereas the vertical height of the nanostructures remained almost similar, as clearly shown by the AFM images and cross-sectional line profiles in Figure 8d–d-2. After increasing the $T_a$ further, i.e., up to 900 °C, the evolution of isolated NPs occurred mildly, as observed in Figure 8e,f. In the high-$T_a$ regime, the elongated shape of NPs gradually became semispherical with improved uniformity and spacing, which is also shown by the reduced FFT patterns. $R_q$ and SAR summary plots of the isolated NPs also showed minor increments with temperature. In this set, the shape, spacing, and size uniformity of the NPs were much improved compared to the pure Pt dewetting due to the concurrent influence of alloying and sublimation [24]. The evolution of pure Pt NPs at high $T_a$ was further confirmed by the elemental analysis of NPs at 900 °C, as shown in Figure 9g–l. The elemental phase maps and EDS line profile clearly show the presence of only Pt in the NP region.
Figure 8. Evolution of the medium-sized Ag–Pt and Pt NPs on sapphire (0001) from the Ag$_{15}$nm/Pt$_{7.5}$nm bilayers annealed between 500 and 900 °C for 120 s. (a–f) AFM top-views (3 × 3 μm$^2$) with FFT power spectra as insets. (a-1–f-1) Enlarged AFM side-views (750 × 750 nm$^2$). (a-2–f-2) Cross-sectional line profiles. (g) Summary plots of $R_q$ and the SAR. (h) Plots of Pt M$_{\alpha 1}$ and Ag L$_{\alpha 1}$ counted as a function of annealing temperature. (i) EDS spectra of the samples annealed at 500, 550, 600, and 900 °C.
Figure 9. Elemental analysis of the Ag–Pt and Pt NPs fabricated at 550 and 900 °C from the Ag_{15 nm}/Pt_{7.5 nm} bilayers. (a–d) SEM image and Pt, Ag, and Al phase maps of the Ag–Pt alloy nanoclusters on sapphire at 550 °C. (e,f) Corresponding enlarged SEM image and the EDS line profile at 550 °C. The nanocluster region shows the overlapping of Ag and Pt elemental lines due to the homogeneous distribution of Ag and Pt atoms in the nanoclusters. (g–j) SEM image and Pt, Al, and O map of the sample at 900 °C. (k,l) Enlarged Pt NPs and elemental line profiles through the NPs. The NPs only show a strong Pt line, while the Ag line is similar to the background signal, which clearly indicates that the Ag atoms were completely sublimated at high temperatures.

The LSPR properties of medium-sized Ag–Pt and Pt NPs fabricated with the Ag_{15 nm}/Pt_{7.5 nm} bilayers are summarized in Figure 10, and the e-field profile of typical NPs is shown in Figure A8. First of all, the extinction spectra demonstrated two different spectral shapes, as presented in Figure 10a–a-3: i.e., the Ag–Pt between 500 and 600 °C and Pt NPs above 650 °C, which again could have been due to Ag sublimation and size reduction. The absorption peaks were gradually attenuated along with the increased $Ta$ between 500 and 900 °C, as shown in Figure 10a–a-3. Since the Ag–Pt nanoclusters were generally bigger than 300 nm in this set, the extinction peaks in the UV (~300 nm) and VIS regions (~500 nm) could be assigned to the excitation of higher-order and multipolar resonance modes, respectively [35]. The simulated e-field and extinction spectra of typical Ag–Pt and Pt NPs are shown in Figure A8, which exhibits the strong e-field confinement at the boundary of the NPs in both cases. Strong multipolar resonance peaks were observed in the VIS region for large-sized Ag–Pt and Pt NPs. However, extinction peaks were observed at a slightly longer wavelength in the simulated spectra compared to the measured one. In this set, the VIS resonance peak normally had less intensity compared to the first set, which could have been due to the smaller average size and reduced Ag
The width of the multipolar resonance peak was found to be narrowed, as presented in Figure 10a-3, along with the improvement of NP uniformity [32]. For the isolated Pt NPs between 650 and 900 °C, the intensity of the multipolar peak was slightly enhanced, as shown in Figure 10a-2, as the average size of the Pt NPs increased due to enhanced atomic diffusion. Likewise, the e-field of the Pt NPs was also enhanced, and the extinction peak was narrowed, as seen in Figure A8e–h.

Figure 10. Localized surface plasmon resonance (LSPR) properties of the Ag–Pt and Pt NPs fabricated with the Ag15 nm/Pt7.5 nm bilayer films between 500 and 900 °C. (a–a-3) Extinction and normalized extinction spectra. (b–b-2) Reflectance and normalized reflectance spectra. (c–c-3) Transmittance and normalized transmittance spectra. (d) Plots of average reflectance and transmittance.
In terms of the reflectance spectra presented in Figure 10b–b-2, the absorption dip of Ag–Pt nanoclusters was gradually reduced with the increased Ta between 500 and 600 °C due to Ag sublimation. Consequently, the absorption dip completely vanished, and a shoulder was formed in the UV-VIS region, with the isolated Pt NPs between 650 and 900 °C, which could have been due to the strong backscattering of Pt NPs. This further indicated the development of stronger dipolar resonance along with the smaller size of NPs. The transmittance spectra generally revealed a flat response with the Ag–Pt NPs and VIS dip with the Pt NPs (Figure 10c). Since the Ag–Pt nanoclusters were generally large, the high forward scattering could cause a flat spectral response in the transmittance spectra. However, it was also observed that the absorption dip started to develop at ~500 nm, as shown in Figure 10c-1, along with the evolution of isolated and relatively smaller-sized NPs. In the case of relatively smaller Pt NPs, they generally showed absorption dips at ~520 nm, as presented in Figure 10c-2, which could have been due to the shifting of the resonance mode from quadrupolar to dipolar. As the uniformity of the Pt NPs improved between 650 and 900 °C, the absorption dip was enhanced and became narrower, as seen in Figure 10c-3. In the case of average reflectance and transmittance, they showed an opposite trend (along with the surface coverage change of NPs) (Figure 10d).

4. Conclusions

In summary, the fabrication of Ag–Pt and Pt NPs of various sizes and configurations and their corresponding LSPR properties was successfully demonstrated on sapphire (0001) via the solid-state dewetting of three distinctive Ag–Pt bilayers. Particularly, two different growth regimes were commonly observed through control over the annealing temperature (Ta), such as the gradual evolution of larger Ag–Pt nanoclusters below 600 °C and isolated Pt NPs above 650 °C. The dynamic LSPR properties of the corresponding Ag–Pt and Pt nanostructures were revealed in the UV and VIS regions through an analysis of the extinction, reflectance, and transmittance spectra as well as FDTD simulations. The Ag–Pt NPs exhibited strong absorption bands in the UV and VIS regions, while the Pt NPs showed mild LSPR absorption. Along with the increased temperature, the intensity, position, and width of the absorption bands were readily varied due to the gradual sublimation of Ag and the evolution of nanostructures from connected to isolated morphology. These resulting NPs were contrasted with previously studied pure Pt NPs and were found to be distinct in terms of size, shape, and uniformity even under identical growth conditions. For instance, the pure Pt NPs at high temperatures were significantly larger, more isolated, and more regular compared to those obtained with the pure Pt films.

Author Contributions: S.P., S.K., and P.P. participated in the experimental design and carried out the experiments. S.P., S.K., and P.P. participated in the data analysis. P.P. and J.L. designed the experiments and testing methods. S.P., S.K., and J.L. carried out the writing. All authors helped in drafting and have read and approved of the final manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Figure A1 shows a detailed morphological and optical characterization of bare sapphire (0001) after degassing and prior to the deposition of metallic thin films. The surface height of the bare sapphire was less than 1 nm after degassing. In the optical spectra, the bare sapphire exhibited no wavelength dependency between 250 and 1100 nm.
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Figures A2 and A3 describe the systematic evolution of large-sized Ag–Pt and Pt NPs on sapphire with the Ag$_{70 \text{nm}}$/Pt$_{15 \text{nm}}$ bilayers. The large-scale AFM images along with the cross-sectional line profile in Figure A2 provide a detailed overview of the surface morphology evolution with temperature. The EDS spectra of each sample at a specific temperature show the elements and their atomic ratios in Figure A3. In Figure A4, FDTD-simulated extinction spectra with corresponding typical AFM images are presented.
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Figure A2. Evolution of the network-like Ag–Pt and isolated Pt NPs with the Ag\textsubscript{70 nm}/Pt\textsubscript{15 nm} bilayers through control over the annealing temperature between 500 and 900 °C. (a–i) AFM side-views (5 × 5 \( \mu \)m\(^2\)). (a-1–i-1) Corresponding cross-sectional line profiles.
Figure A3. EDS spectra (a-i) of the Ag–Pt and Pt nanostructures fabricated with the Ag\textsubscript{70 nm}/Pt\textsubscript{15 nm} bilayers between 500 and 900 °C. The insets show enlarged Pt M\textsubscript{α1} and Ag L\textsubscript{α1} peaks between 2 and 4 keV and the atomic weight % (wt %) and atomic % (at %) of elements.
Figure A4. (a,c) Simulated extinction power spectra and typical Ag–Pt and Pt NPs (shown in (b,d)). The typical AFM images were imported into the structure space using surface import. The structure was excited by the total field-scattered field (TFSF) source from the z direction, and the absorption and scattering power were monitored. Finally, the extinction was calculated by summing up the absorption and scattering power. For the simulation, the perfectly matched layer (PML) boundary condition was applied in all directions, in which the minimum distance between the PML boundary and the structure was greater than 500 nm. The dielectric constant from Palik’s model was utilized for the pure Pt NPs, while for pure Ag, Rakic’s model was used. For the Ag–Pt alloy compositions, the dielectric constants were determined based on the weighted average of dielectric constants from pure Ag and Pt.

Figure A5 presents a general overview of AFM images, enlarged 3D side-views, and cross-sectional profiles for the small-sized Ag–Pt and Pt NPs fabricated with the Ag_{2.8 nm}/Pt_{0.6 nm} bilayers. Figures A6–A8 present large-scale AFM images, cross-sectional line profiles, full-scale EDS spectra, and FDTD-simulated e-field and extinction spectra for the Ag–Pt and Pt NPs fabricated with the Ag_{15 nm}/Pt_{7.5 nm} bilayers.
Figure A5. Small and densely packed Ag–Pt and Pt NPs formed on sapphire (0001) through the annealing of Ag$_{2.8}$ nm/Pt$_{0.6}$ nm bilayers between 500 and 800 $^\circ$C. (a–f) AFM top-views (700 x 700 nm$^2$). Insets show the magnified AFM top-views of 100 x 100 nm$^2$. (a-1–f-1) Corresponding color-coded AFM side-views of 100 x 100 nm$^2$. (a-2–f-2) Cross-sectional line profiles.
Figure A6. AFM side-views of the Ag–Pt and Pt NPs formed between 500 and 900 °C with the Ag$_{15}$ nm/Pt$_{7.5}$ nm bilayers. (a–i) AFM side-views (3 × 3 μm$^2$). (a-1–i-1) Corresponding cross-sectional line profiles.
Figure A7. EDS spectral analysis (a–i) of the various Ag–Pt and Pt nanostructures fabricated between 500 and 900 °C with the Ag$_{15}$ nm/Pt$_{7.5}$ nm bilayers. Atomic weight (wt) % and atomic (at) % of elements and enlarged spectra to show the Pt and Ag peaks (insets).
Figure A8. FDTD simulations of the medium-sized Ag–Pt and Pt NPs fabricated with the Ag\textsubscript{15 nm}/Pt\textsubscript{7.5 nm} bilayers at 600 and 900 °C. (a,e) AFM image of typical NP along with cross-sectional line profiles. (b,f) E-field top-views in $x$–$y$ plane. (c,g) Corresponding line profiles at specific locations. (d,h) Simulated extinction power spectra of corresponding Ag–Pt and Pt NPs.

Figures A9–A13 show the evolution of the Ag–Pt alloy and patterned Pt NPs on sapphire with the Ag\textsubscript{30 nm}/Pt\textsubscript{15 nm} bilayers through control over the annealing temperature. In general, the partially dewetted and connected nanostructures were observed at a low annealing temperature, and well-patterned nanostructures formed at higher annealing temperatures. Initially, few overgrown nanostructures and voids were formed at 500 °C because of the limited interdiffusion atoms and low dewetting extent of the bilayer film. The AFM side-view and SEM images presented in Figures A9 and A10 clearly demonstrate this. The depth of the void was nearly ~70 nm, as clearly shown by the cross-sectional line profile in Figure A9a-1. As the annealing temperature increased to 600 °C,
connected network-like nanostructures were observed, as shown in Figure A9c-1. This could have been due to the slightly increased alloying and the diffusion of atoms in the alloyed phase. The line profile presented in Figure A9c-1 indicates that the height of the nanostructures increased to ~80 nm. When the annealing temperature increased to 650 °C, a drastic evolution in the nanostructures was observed. Isolated NPs were formed, and they were organized in a patterned form. The isolated NPs could be referred to as monometallic Pt NPs due to the extensive sublimation of Ag atoms, as observed in the previous sets. Furthermore, the patterned Pt NPs remained consistent even when the annealing temperature was increased to 750 and 800 °C. At a high annealing temperature of 900 °C, the Pt NPs were well separated and randomly oriented, as shown in Figure A9i-1. The pattern of the NPs was lost at high annealing temperatures, which could have been due to the extensive sublimation of Ag atoms and the strong agglomeration of the Pt atoms. This led to the formation of larger-sized Pt NPs, as clearly shown by the cross-sectional line profile. Generally, \( R_q \) increased at low annealing temperatures between 500 and 600 °C due to the sharp increase in the height of the nanostructures. As the temperature increased, the \( R_q \) value also rose and fell at annealing temperatures between 650 and 900 °C due to the formation of pattern nanostructures with varying heights. Similarly to \( R_q \), the SAR increased up to 650 °C, while it rose and fell at annealing temperatures between 650 and 900 °C. The EDS spectra presented in supplemental Figure A8 clearly demonstrate the mild sublimation of Ag atoms at low temperatures (below 600 °C) and extensive sublimation between 650 and 900 °C.
Figure A9. Self-assembled Ag–Pt and Pt NPs on sapphire (0001) with the Ag$_{30}$ nm/Pt$_{15}$ nm bilayers. (a–i) AFM side-views (5 × 5 μm$^2$). (a-1–i-1) Corresponding cross-sectional line profiles.
Figure A10. SEM images (a–i) of Ag–Pt and Pt nanostructures fabricated with the Ag\text{30 nm}/Pt\text{15 nm} bilayers at annealing temperatures, as labeled.
Figure A11. EDS spectral analysis (a–i) of the various Ag–Pt and Pt nanostructures fabricated with the Ag$_{30}$ nm/Pt$_{15}$ nm bilayers. Insets are the atomic wt % and at % of elements, and enlarged spectra between 2 and 4 keV show the Ag and Pt peaks.
Figure A12. Optical properties of the Ag–Pt and Pt nanostructures fabricated with the Ag$_{30}$ nm/Pt$_{15}$ nm bilayers between 500 and 900 °C. (a) Extinction spectra. (a-1,a-2) Normalized extinction spectra. (a-3) Enlarged extinction peak in the VIS region to show the distinct peak behavior with the morphology of NPs at different annealing temperatures. (b) Reflectance spectra. (b-1,b-2) Normalized reflectance spectra. (b-3) Enlarged reflectance dip. (c) Original transmittance spectra. (c-1,c-2) Normalized transmittance spectra. (d) Plots of average reflectance and transmittance.
Figure A13. Formation of self-assembled Ag–Pt NPs on sapphire (0001) through control over the annealing duration (between 0 and 60 s). The composition of the bilayer was Ag$_{7}$ nm/Pt$_{1.5}$ nm, and it was annealed at 350 °C. (a–c) AFM top-views (1 × 1 µm$^2$). (a-1–c-1) Cross-sectional line profiles. (a-2–c-2) AFM side-views (1 × 1 µm$^2$). After 60 s, the ripening was saturated. (d–f) Corresponding extinction, reflectance and transmittance spectra.

Table A1. Summary of $R_q$ and the SAR of various Ag–Pt nanostructures on sapphire through control over the annealing temperature (between 500 and 900 °C) with three different bilayer films: Ag$_{70}$ nm/Pt$_{15}$ nm, Ag$_{2.8}$ nm/Pt$_{0.6}$ nm, and Ag$_{15}$ nm/Pt$_{7.5}$ nm.

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Table A2. Summary of average reflectance and transmittance of Ag–Pt nanostructures as a function of annealing temperature for three different bilayer films: Ag\textsubscript{70 nm}/Pt\textsubscript{15 nm}, Ag\textsubscript{2.8 nm}/Pt\textsubscript{0.6 nm}, and Ag\textsubscript{15 nm}/Pt\textsubscript{7.5 nm}.

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