Refining laser-induced dewetting for bimetallic Au–Pd nanoparticle synthesis on ZnO thin films: Optimizing fluence for substrate integrity


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Refining laser-induced dewetting for bimetallic Au–Pd nanoparticle synthesis on ZnO thin films: Optimizing fluence for substrate integrity

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ABSTRACT

We report the fabrication of metal alloy Au–Pd nanoparticles on semiconductor thin film substrates (ZnO) by laser-induced dewetting. Employing a UV excimer laser, a single pulse was directed onto a three-layer film stack on a glass substrate: glass/ZnO/Au/Pd and glass/ZnO/Pd/Au. We simulated the temperature attained by the thin films enabling the prediction of energy thresholds required for melting the metal films but avoiding modifying the ZnO film. A specific range is reported of the pulse energy conducive to nanoparticle formation and the energy threshold required to modify the ZnO film beneath them. Depending on the pulse energy applied, the mean diameter of the nanoparticles varied from approximately 150 to around 70 nm. Notably, higher fluences resulted in smaller particles but also induced surface cracks in the ZnO film. Additionally, we observed a reduction in nanoparticle size with increased Pd content. Our results show that laser-induced dewetting can produce bimetallic alloy nanoparticles and, at the same time, ensure the preservation of the optical properties of the ZnO film. This approach opens avenues for tailoring material characteristics and expanding the range of applications of metal nanoparticles on semiconductor-based systems.

Key words: nanoparticles, laser-induced dewetting, ZnO film, bimetallic nanoparticles

1. INTRODUCTION

Pulsed laser-induced dewetting of thin films is a simple and flexible technique to form high purity metal nanoparticles (NPs) directly on a surface.1–3 It has been used to fabricate NPs for diverse applications such as photonic devices,4 photocatalysis,5 and sensors,6 among others. Dewetting is a process that results in the formation of NPs adhered to a substrate, which sets it apart from other techniques such as chemical synthesis or laser ablation in liquids which produce colloidal NPs. The formation of NPs through dewetting requires a laser fluence enough to induce melting of a predeposited film on a dielectric or semiconductor substrate. The molten film tends to form discontinuous morphologies such as droplets and islands to minimize the total surface energy within the system. This energy encompasses the surface of the film as well as the substrate and the interface connecting them.7 Once the laser pulse ends, the droplets solidify, forming nanoparticles. For pulses in
the range of nanoseconds or even shorter, it is viable to utilize a substrate composed of a low melting point material. This is possible because the heat diffusion is limited within a few superficial layers of the irradiated region on the substrate.

Several works about laser-induced dewetting have been reported since the early 2000s, with a predominant emphasis on generating noble metals NPs and in studying the physical mechanisms involved in their formation. Most of these investigations center around the production of NPs on bulk substrates, with a notable focus on materials like silicon wafers and glasses. Nevertheless, some applications require producing NPs affixed to thin films instead of bulk substrates. In such cases, the complexities of the formation process increase as heat diffusion and temperature gradients are directly impacted by the thickness of the film and its thermodynamic properties. The presence of a thin film as a substrate introduces additional factors that impact the characteristics of the formed NPs such as size, size distribution, and contact angle, among others. Then, it is imperative to carefully consider the thermodynamic properties of both, the film and the substrate, to ensure the desired functionality and performance of the NPs. Some works have already shown the capability of laser-induced dewetting as viable to produce metal NPs on a thin film made of temperature-sensitive materials without affecting the properties of the underlying film. Beliatis et al. fabricated Au NPs on thin films made of conductive polymers for their application in organic solar cells. Censabella et al. induced dewetting of Pt–Pd bilayers on fluorine-doped tin oxide (FTO). Since the thermodynamic properties of the film and the substrate significantly influence the overall thermal behavior, each metal-film-substrate system requires the appropriate adjustment of the laser parameters to fabricate NPs with desired sizes, shapes, and distributions on thin films.

In recent years, laser-induced dewetting has also been applied for the fabrication of bimetallic NPs. This strategy harnesses the combined benefits of the unique chemical and physical characteristics of two separate metals, leading to synergistic outcomes. For example, bimetallic NPs made of Au–Pd and Ag–Pd have simultaneously plasmonic and catalytic properties, which extend its performance on specific applications. An effective approach for fabricating bimetallic NPs using laser-induced dewetting involves irradiating a stack of two thin films. When the films consist of immiscible metals, dewetting yields solid-solution alloy NPs, whereas immiscible metals lead to phase segregation within the NPs. In addition to this, the relative proportion of the metals in the NPs can be controlled by changing the thickness of each thin film. However, various aspects related with the configuration of the films system, such as the stacking order and the thickness of each film, play an important role in the dewetting and, thus, in the characteristics of the resulting NPs. Moreover, if the substrate on which the bimetallic NPs are formed is itself a thin film deposited on a glass or a silicon wafer, the complexity of a three-layered system must be considered. Consequently, to precisely regulate the composition of the NPs, manage the spatial distribution of the metal within them, and prevent damage to the substrate made of a thin film, it is imperative to configure the geometry of the film stack.

In this work, we employ nanosecond laser irradiation to fabricate bimetallic Au–Pd NPs on a ZnO thin film. For this, we first deposited sequentially thin films of Au followed by Pd (and vice versa) on a ZnO thin film previously deposited on glass. Then, we irradiated the three-layered film with only one laser pulse to produce the bimetallic NPs on the ZnO film. The choice of ZnO as the underlying film is due to its excellent optoelectronic and electrical properties. It is a wide bandgap semiconductor, which has shown good performance as a photocatalyst. The combination of semiconductors with bimetallic NPs has demonstrated an important increase of the photocatalytic activity when comparing with the semiconductor alone. Moreover, bimetallic Au–Pd have demonstrated to have increased catalysts reaction rates than their monometallic versions. To determine the laser pulse energy enough to produce Au–Pd NPs without damaging the underlying ZnO film, we simulated the temperature of the ZnO film and the bilayer systems ZnO + Pd and ZnO + Au. By choosing the proper values of the fluence, film thickness, and stacking order of the metal layers, we control the size of the NPs while preserving the transmittance of the underlying ZnO film.

2. EXPERIMENTAL SETUP

The Au–Pd bimetallic NPs were formed on a ZnO thin film through the single-pulse irradiation of a three-layered film stack as shown in Fig. 1. Two different sequences of the deposition of the Pd and Au layers were analyzed: one with Pd as the top layer and Au as the bottom film, and the other with the reverse order, but always maintaining the ZnO film as substrate. The thickness of the ZnO layer was kept fixed, while the thicknesses of the metal layers (hAu and hPd) were varied to obtain NPs of different compositions. All the configurations were irradiated by one laser pulse. Each stage of the experiments is described below.

2.1 Thin film deposition

Three-layered films were grown on glass substrates (Corning 7049) by sequential deposition in two configurations: (1) ZnO deposition followed by Au deposition, followed by Pd deposition and (2) ZnO deposition followed by Pd deposition followed by Au. RF magnetron sputtering was used for ZnO films deposition on glass substrates at a temperature of 400 °C; the target was a 99.9% pure ZnO disk sputtered at 60 W of power. The base pressure was 8 × 10⁻⁶ Pa and the deposition was performed at 0.6 Pa of 80% Ar and 20% O₂ atmosphere at a flow rate of 28 and 7 SCCM, respectively. The deposition time of ZnO films was kept fixed at 60 min for all experiments (after a presupersputtering time of 3 min), resulting in ZnO films of hZnO = 158 ± 28 nm in thickness.

Deposition of the metal films was performed by direct current sputtering of high purity targets, on the ZnO films described above. All depositions were carried out under an Ar atmosphere at 5 Pa with a current of 25 mA. The total deposition time was set at 60 s. The thickness of the monometallic films, which was measured by means of an optical profilometer, was hAu = 13.7 ± 3.6 nm for Au films and hPd = 13.0 ± 1.7 nm for Pd films. The roughness of these monometallic films was measured by atomic force microscopy, resulting in 2.7 and 3.7 nm, respectively.

The bilayer films of Au–Pd and Pd–Au were meticulously prepared in a sequential manner. Specifically, a duration of t₁ seconds was allocated to Pd deposition, followed by t₂ seconds for Au deposition (and vice versa), ensuring that t₁ + t₂ = 60 s in all the cases.
Since the relative deposition times of Au and Pd were systematically varied in increments of 25%, we named the samples using the name of the metal element followed by the percentage of the deposition time. For instance, a three-layered film named ZnO–Au25–Pd75 signifies a ZnO/Au/Pd film stack on glass with ZnO at the base and Pd on top, where the deposition times for Au and Pd were 25% of 60 s (15 s) and 75% of 60 s (45 s), respectively.

2.2 NPs formation by laser irradiation

The experimental setup for the irradiation of the films has been described elsewhere. Briefly, the film stacks were irradiated with an excimer laser, emitting pulses at 248 nm wavelength and 25 ns of duration, in air at atmospheric pressure. The laser pulses passed through a homogenizer to obtain a top hat beam profile that was focused with a positive lens. The samples were mounted on a X-Y-Z translation stage and exposed to only one pulse with a uniform spot of 0.059 ± 0.001 cm² of circular area. The pulse energy varied from 3 to 22 mJ in increments of 2 mJ; thus, the fluence ranged from 51 to 373 mJ/cm² in increments of 33.8 mJ/cm².

To analyze changes in the optical properties of the films before and after irradiation with different laser energies, we estimated the transmitted light intensity ratio $I_{Tr}$. This intensity corresponds to the ratio between the light intensity that exits a sample after being illuminated with a deuterium-halogen lamp and that which exits a clean glass substrate. The lamp, coupled with an optical fiber, illuminated the sample at normal incidence, and the transmitted light was directed by a second optical fiber to a spectrometer. This calculation is expressed as $I_{Tr} = S_t - D_t/R_t$, where $S_t$ is the intensity emerging from the films stack deposited on the glass, $R_t$ is the intensity emerging of a glass substrate, and $D_t$ is the intensity of the background (with the lamp turned off). The measurement of $I_{Tr}$ allowed us to analyze changes produced on the samples resulting from pulse irradiation. However, it is important to note that this calculation does not correspond to the transmittance since reflectance was not considered.

The surface morphology of both, as grown and irradiated areas, were analyzed by scanning electron microscopy (SEM) using a Jeol 7600 F field emission-scanning electron microscope. The images were processed using Image J software to measure the diameter of the nanoparticles. A selected set of samples was analyzed by x-ray diffraction using a Rigaku Ultima IV with a Cu lamp ($K\alpha$ radiation with a wavelength of 1.541 Å). The measurements were performed at an incidence angle of 1°, step of 0.02°, and scan speed of 1° min⁻¹.

2.3 Simulation

The temperature of each layer of the film stack was simulated by COMSOL. These data were used to estimate the laser fluence needed to melt the metal films and, thus, to produce the nanoparticles and to delimit the threshold fluence to damage the ZnO layer. The interaction between the laser pulse and the monometallic films was simulated solving the heat equation using the finite element method (COMSOL).

$$C_p \rho \frac{\partial T}{\partial t} - \nabla \cdot (k_c \nabla T) = Q,$$

$$Q = aP_{laser} (1 - R) \Phi(t) = aP_{laser} \frac{(1 - R)}{\sqrt{2\pi\sigma}} \exp \left( -\frac{(t - t_d)^2}{2\sigma} \right),$$

where $C_p$ is the specific heat at constant pressure, $\rho$ is the density, $k_c$ is the thermal conductivity, $t$ is the time, $T$ is the temperature that depends on position $t$, and $Q$ is the heat source. The source term represents a top-hat beam profile, where $\Phi(t)$ is the temporal profile of the pulse (a gaussian profile), $P_{laser}$ is the laser power, $R$ is...
the reflectivity of the top layer, $t_d$ is a delay time representing the maximum of the temporal gaussian profile of the laser pulse (40 ns), $\sigma = \tau_p/2.35482$, where $\tau_p$ is the FWHM of the pulse (25 ns), and $\alpha$ is the absorption coefficient.

The simulation was conducted on a small volume with dimensions of XYZ, measuring 100 nm $\times$ 100 nm $\times$ h, where h represents the thickness of the respective film (Au, Pd, or ZnO). The glass substrate was assumed to have a thickness of 1 $\mu$m. This volume represents the central region irradiated by the laser pulse. To leverage the symmetry of the problem, a different mesh was employed for each layer (see Fig. S1). The simulation was spanned from 0 to 100 ns, utilizing a time step of 0.01 ns. A second interval from 100 ns onward, using a time step of 1 ns was calculated for selected pulse energies. The relative tolerance used for all simulations in this study was set to $1 \times 10^{-6}$.

The temperature was simulated over time at different positions within the film stack, as illustrated in Fig. 2(a). For monometallic films, the position was calculated at half the metal film height (red point). In contrast, for the ZnO film, temperature calculations were performed at three specific positions (blue points): the top (1 nm below the metal film-ZnO interface), the midpoint, and the bottom (1 nm above the ZnO-glass interface). The temperature of the glass substrate was calculated 10 nm below the ZnO-glass interface (green point). The physical parameters considered for the simulation are listed in Table I.

3. RESULTS AND DISCUSSION

3.1. Temperature simulation

Figure 2(b) shows the simulated temperature profile of a Pd and ZnO film stack on a glass substrate when irradiated with a 9 mJ pulse. The temperature evolution aligns with previous findings for metal thin films and nanoparticles under ns-pulsed laser irradiation. Initially, each layer’s temperature sharply rises at the pulse onset, levels out during phase changes, and then rises again. The maximum temperature is reached at different times depending on the position. The timing of reaching maximum temperature varies by layer. The Pd film, directly hit by the pulse, reaches its peak temperature during the laser pulse, while the ZnO layer and glass substrate achieve their maxima later due to heat conduction. Subsequently, the maximum temperature decreases at a slower rate than heating, returning to room temperature around 6 $\mu$s (see Fig. S2).

Figure 3 shows the maximum temperature reached by each layer of the film stack (Au, Pd, and ZnO) and the glass substrate produced by single-pulse irradiation as a function of pulse energy. Three different configurations are shown: (a) a ZnO “bare” film, (b) a ZnO film + a monometallic film made of Au (ZnO_Au100), and (c) a ZnO film + a monometallic film made of Pd (ZnO_Pd100). Figure 3 also includes a scheme of the phase change of each layer where 0 corresponds to the starting phase (solid) and 1 to the complete melting of the film. The phase transition from solid to liquid of each film was considered over a temperature range in which melt-initiation occurs at the surface and progressive heating produces the movement of a melting front toward the interior of the film until melt-completion. Thus, the phase change threshold can be considered as the one from which the value of the phase change is greater than zero.

As mentioned in the experimental section, the temperature of the ZnO film was calculated at three positions in the films: the top, the midpoint, and the bottom. As expected, the temperature
depends on the position, specifically on the distance from the film surface. For example, when a "bare" ZnO film on glass [Fig. 3(a)] is exposed to a pulse of 10 mJ, the top position reaches 2330 K, the midpoint records 1922 K, and the bottom reaches 1695 K. This means that the upper part of the film undergoes a phase change while the rest maintains its original phase. The simulation indicates that the surface of the ZnO film starts melting at 9 mJ, but complete melting of the entire film of 160 nm in thickness is reached by 16 mJ. The temperature of the surface of the glass is practically the same as the bottom of the ZnO film but the glass substrate undergoes a phase change at 7 mJ. This value is smaller than the energy needed to melt the ZnO because the transition temperature of glass is lower than that for ZnO. Even though the laser pulse does not directly reach the glass surface, the ZnO film absorbs well the incoming radiation ($\alpha = 3.3 \times 10^7 \text{ m}^{-1}$), and then the temperature of the glass increases by heat conduction.

When the ZnO film is covered with a monometallic layer made either by Au or by Pd [Figs. 3(b) and 3(c)], the ZnO film melts at higher fluences in comparison with a "bare" ZnO film. In this case, the laser radiation is absorbed directly by the metal layer producing intraband transitions of the electrons in the conduction band within a skin layer of approximately 10 nm. This is followed by electron-phonon interactions whose energy is dissipated into heat. When considering a constant pulse energy, the temperature attained by the Au layer surpasses that of the Pd layer, as long as the phase change is not attained. Several factors may contribute to this phenomenon. Notably, the reflectivity of the latter is significantly higher, and the thermal conductivity of Au surpasses that of Pd, resulting in a more rapid dissipation of heat. In addition, the heat capacity of Au is lower than that for Pd; thus, the former requires less energy to increase its temperature by 1°. For example, for a pulse of 10 mJ, the temperature of the Au layer is approximately 2190 K while the Pd film is around 1860 K. The energy thresholds to melt the Au film and Pd film were estimated by the simulation being approximately 4 and 6 mJ, respectively. It should be noted that the melting point of these films was not the value for the bulk material but a film of approximately 10 nm in thickness.\textsuperscript{29,30} The temperature of the superficial layers of the ZnO film below the metal layer is almost the same as the metal film. Due to the proximity of the optical penetration depth of Au and Pd at a 248 nm to the thickness of the films, a considerable portion of the laser intensity is able to reach the ZnO film. Thus, the temperature of the ZnO film increases by both heat conduction and by absorption of the portion of the laser pulse which passes through the metal layer. With an Au film on top, the surface layers of the ZnO film start melting at 10 mJ, but the film melts completely at 19 mJ, while with a Pd on top, melting starts at 12 mJ and completes at 23 mJ. The semi-infinite glass substrate again reaches a higher temperature when the top layer is made of Au. For example, for irradiation at 10 mJ, the temperatures of the surface of the glass are approximately 1475 and 1330 K for Au and Pd as the top layer, respectively. As mentioned above, the causes of this difference in the temperature of the films stack are the reflectivity of the top layer and the difference between the heat capacity and thermal conductivity of Au and Pd.

### TABLE I. Physical parameters for soda lime glass and ZnO, Pd, and Au (Refs. 11, 20, and 26–32).

<table>
<thead>
<tr>
<th>Property</th>
<th>Soda lime glass</th>
<th>ZnO</th>
<th>Pd</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>0.09</td>
<td>62</td>
<td>72</td>
<td>317</td>
</tr>
<tr>
<td>Specific heat capacity (J/kg K)</td>
<td>880</td>
<td>506</td>
<td>243</td>
<td>129</td>
</tr>
<tr>
<td>Melting temperature (K)</td>
<td>1288</td>
<td>2098</td>
<td>1250</td>
<td>1061</td>
</tr>
<tr>
<td>Evaporation point (K)</td>
<td></td>
<td></td>
<td>2963</td>
<td>1676</td>
</tr>
<tr>
<td>Softening temperature (K)</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractive index at 248 nm</td>
<td>$n = 1.5539$</td>
<td>$n = 1.0733$</td>
<td>$n = 1.3284$</td>
<td></td>
</tr>
<tr>
<td>$k = 0.000 \ 049 \ 9 \ (at \ 310 \ nm)$</td>
<td>$k = 1.9833$</td>
<td>$k = 1.6226$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reflectivity (% at 248 nm)</td>
<td></td>
<td>45</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Optical penetration length at 248 nm (nm)</td>
<td>9.455 $\times 10^3$</td>
<td>3.3 $\times 10^7$</td>
<td>1.0585 $\times 10^4$</td>
<td>8.2217 $\times 10^7$</td>
</tr>
</tbody>
</table>

3.2 Irradiation of ZnO films

As a first step, we analyzed the effect of the single-pulse irradiation on ZnO films without any further metal deposition. Since our goal is to decorate ZnO films with mono- and bimetallic NPs for further applications, it is desirable to know if the irradiation induces changes in the physical properties of the semiconductor film. ZnO absorbs very well the 248 nm having an optical absorption coefficient of $3.3 \times 10^7 \text{ m}^{-1}$; thus, as previously reported,\textsuperscript{26–28} the surface morphology, crystalline structure, and optical and electrical properties of ZnO films can be modified as a result of laser irradiation with UV wavelengths. These films appeared to be polycrystalline, with a hexagonal wurtzite structure oriented along main planes as revealed for the clear presence of (002), (101), (102), and (103) peaks (see Fig. S4,\textsuperscript{46} the spectrum ZnO before irradiation). However, the most prominent growth occurred along the c-axis (002).

Figure 4 shows SEM images of a ZnO film before and after irradiation at three representative laser pulse energies. The as-grown ZnO film [Fig. 4(a)] shows a uniform surface morphology with observable grains in their entire surface. A similar morphology can be observed for the film irradiated at 7 mJ [Fig. 4(b)], which apparently remains unaffected after the action of the laser pulse. In contrast, important changes in the surface morphology of the films after irradiation at 13 mJ and higher values are clearly observed [Figs. 4(c) and 4(d)]. For 13 mJ, grains at the surface are
more defined, looking like puzzle pieces; meanwhile, for 21 mJ, the surface looks considerably smoother, but in both cases, cracks are present along the entire images. The regions divided by the cracks span several micrometers, exceeding the thickness of the ZnO film. A similar surface morphology of ZnO:Au films irradiated with UV laser pulses has been reported by Charpentier et al., who explained the presence of cracks as a consequence of melting and recrystallization after a certain energy threshold. The recrystallization accompanied by contraction lead the crack formation. This explanation is reasonable because ZnO films absorb wavelengths below 380 nm very well. The optical penetration depth of ZnO at 248 nm is approximately 12 nm (see Table I); then, the upper layers of the ZnO film interact directly with the laser pulse, increasing their temperature, and the entire film is heated by conduction. As the pulse energy increases, both the maximum reached temperature and the thickness of the melted top layer also increase. Then, recrystallization and contraction are expected to occur for the highest fluences.

To determine the energy threshold to modify the ZnO films when they are directly irradiated (without a metal film), we compared the transmitted light intensity ratio $I_{Tr}$ of the films before and after irradiation at different pulse energies. The mean value of $I_{Tr}$ of the as-grown films, calculated in the range of 450–850 nm, was $0.84 \pm 0.04$. This value was not affected by irradiation at low pulse energies, but after one pulse irradiation at 10 mJ, it decreases monotonically as the pulse energy increases (see Fig. S3). The film irradiated at 21 mJ showed a value of $I_{Tr} = 0.54 \pm 0.06$. This could be observed with the naked eye; the samples look darker as the energy increases. The decrease of the optical transparency is a consequence of light scattering produced by the presence of grain boundaries in the crystalline films and the creation of oxygen defects in the structure, both promoted by laser irradiation. Since the samples irradiated at energies below 10 mJ do not show changes in $I_{Tr}$, we considered this value as the energy threshold for

![FIG. 3. Simulated maximum temperature and phase change coefficient for each layer as a function of the pulse energy for the cases: (a) a “bare” ZnO film, (b) ZnO_Au100 film, and (c) ZnO_Pd100 film, all on glass. The horizontal dotted lines correspond to the temperature of phase change.](image)

![FIG. 4. SEM images of surface ZnO thin film (a) as grown and after irradiation at (b) 7, (c) 13, and (d) 21 mJ.](image)
the modification of ZnO films. This experimentally determined threshold value agrees with that obtained by the temperature simulation, which indicates that the upper section of the ZnO film initiates melting at a threshold energy of 9 mJ.

3.3 Irradiation of ZnO/metal 1/metal 2 films stack

Two types of multilayered samples were fabricated: two-layer and three-layer stacks of films. Table II contains their description and schematic representation. Two-layer samples were made with a ZnO film plus a monometallic Au or Pd film. Three-layer samples were made of a ZnO film plus Au and Pd films deposited in two ordered sequences (three samples with Pd on top and three with Au on top), in which, the relative content of metal was modified by varying the deposition time of the films. The thicknesses of the metal films were determined by analyzing their deposition rates, which were calculated from the thickness of single-metal films deposited over a period of 60–120 s, measured with an optical profilometer. The thickness of the monometallic films deposited during 60 s was 13.7 ± 3.6 nm for Au and 13.0 ± 1.7 nm for Pd. By varying the deposition time of each metal and keeping the total time fixed at 60 s, we modified the relative thickness between Au and Pd. All the samples were irradiated with one laser pulse at different energies from 3 to 21 mJ in steps of 2 mJ.

Figure 5 shows some representative transmitted light intensity ratio of the samples before and after irradiation at different energies. \( I_{Tr} \) spectrum of the pre- and postirradiated samples was measured at the same location to avoid potential inaccuracies arising from nonuniformities within the samples, primarily attributed to variations in the thickness of the underlying ZnO film. It should be considered that these spectra result of the interaction of the ZnO film and the metal film/nanoparticles with the incoming light form the lamp. The spectra start at 370 nm since the underlying ZnO film absorbs very well below that value, making it impossible for us to detect the induced changes in the metal films [see Fig. S3(b)].

For larger values of the wavelength, the most important contribution belongs to the metal. Figures 5(a) and 5(b) show the transmitted light intensity ratio spectra of the ZnO_Au100 and ZnO_Pd100 before and after irradiation at different pulse energies. The as-prepared Au film [black line in Fig. 5(a)] shows a maximum before 600 nm, which corresponds to the overlap of the intra- and interband transitions. \( I_{Tr} \) spectra, and it produces a well-defined minimum between 600 and 700 nm, which can be attributed to an absorption

Table II. Schematic representation of the samples to be irradiated, which shows the sequence of the Pd and Au layers deposited on a ZnO film and deposition time for each metal. The name of each sample corresponds to the percentage of the deposition time where the total time corresponds to 60 s. The thickness was calculated from the deposition rate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scheme</th>
<th>Top layer metal</th>
<th>Deposition time (s)</th>
<th>Calculated thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Au</td>
<td>Pd</td>
</tr>
<tr>
<td>ZnO</td>
<td>None</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ZnO_Au100</td>
<td></td>
<td>Au</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>ZnO_Au75Pd25</td>
<td></td>
<td>Pd</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>ZnO_Pd25Au75</td>
<td></td>
<td>Au</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>ZnO_Au50Pd50</td>
<td></td>
<td>Pd</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>ZnO_Pd50Au50</td>
<td></td>
<td>Au</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>ZnO_Au25Pd75</td>
<td></td>
<td>Pd</td>
<td>15</td>
<td>45</td>
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<tr>
<td>ZnO_Pd75Au25</td>
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<td>Au</td>
<td>15</td>
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</tr>
<tr>
<td>ZnO_Pd100</td>
<td></td>
<td>Pd</td>
<td>0</td>
<td>60</td>
</tr>
</tbody>
</table>

*Measured thicknesses.*
band due to dipolar surface plasmon resonance (SPR); it suggests the formation of nanoparticles as it will be confirmed later by SEM images. In contrast, the preirradiated Pd film shows a monotonically increasing contribution in almost the whole observed wavelength range. This behavior is because the d-electrons overlap the s- and p-electrons. The presence of Pd NPs is not as clear by I\textsubscript{Tr} as that for Au NPs since spherical NPs of Pd exhibit the LSPR in the UV region, which is covered by the absorbance of the ZnO film. However, Pd spherical nanoparticles with diameters above 80 nm show higher order modes (quadrupolar, octopolar, etc.) in the visible region. This is probably the reason for which a minimum around 500 nm is visible in the spectra of the sample after irradiation at 9 and 13 mJ.

Figures 5(c) and 5(d) compare I\textsubscript{Tr} spectra of the ZnO\_Au50Pd50 and ZnO\_Pd50Au50 samples before and after irradiation. The original compositions of the samples are identical; however, they differ in the stacking order of the metals. In the preirradiated samples, a comparable I\textsubscript{Tr} is observed, characterized by a maximum in the 600–700 nm range. This maximum is similar to that shown for the gold film, which can be attributed to inter- and intraband transitions within the film. After irradiation, the transmitted light intensity of the samples with Au on top is very similar to that before irradiation within the 370–650 nm range; for larger wavelengths, it increases with the pulse energy, suggesting the formation of NPs. In contrast, when Pd is the top layer, I\textsubscript{Tr} is different for each condition, revealing that this condition is more sensitive to the pulse energy.

Since the reflectance and optical absorption coefficient are different for Au and Pd (see Table I), it is expected that the energy threshold to produce bimetallic nanoparticles and the characteristic of those NPs depend on the order of the stack. By means of transmitted light intensity ratio spectra, we determined the threshold energy to modify the films and to qualitatively compare the effect of the stack order. The energy threshold was determined as the minimum energy value at which the I\textsubscript{Tr} spectrum undergoes a discernable change following irradiation. As expected, the energy threshold to modify this spectrum depends on both the stacking order and the relative thickness between metal films. The red transmitted light intensity ratio curve in the graphs in Fig. 5 corresponds to this threshold for each sample. A comparison of the energy thresholds of the different samples is shown in Fig. 5(e). It includes the threshold of a single ZnO film (without metal) discussed in the last section. Comparing the energy threshold of the two-layer films (ZnO + one metal), a pulse at 5 mJ (corresponding to 85 mJ/cm\textsuperscript{2}) is enough to modify the optical absorbance of ZnO\_Au100, but a pulse of 7 mJ (119 mJ/cm\textsuperscript{2}) is needed to modify ZnO\_Pd100. These
values match with the energy threshold predicted by the temperature simulation to complete melting the Au and Pd films [see Fig. 3]. The difference between this energy threshold is explained by comparing the values of the reflectivity at normal incidence of both metals; Pd exhibits a reflectivity that is nearly 50% greater than that of Au (see Table I). A second factor to be considered is the metal melting temperature, which is higher for Pd. Thus, higher energy is needed to modify the Pd layer in comparison with Au. A similar result was reported by Schmidl et al. when irradiating Pd and Au films previously deposited on glass. In the case of the three-layer films, the samples with 75% gold content ZnO_Au75Pd15 and ZnO_Pd15Au75 exhibited a difference in the energy density threshold of almost 70 mJ/cm². Notably, the sample with a top layer of Pd required more energy for modification. This difference might be a consequence of the higher reflectivity of the Pd layer at 248 nm than Au; then the incoming laser is more reflected with Pd on top. In contrast, it was found that for the samples containing 50% or less gold content, the energy threshold does not depend on the stacking order. However, the pulse energy was incremented in steps of 2 mJ, equivalent to 34 mJ/cm²; so shorter steps might unveil a potential dependence. Independently of the stacking order, the optical penetration depth at 248 nm in all samples is shorter than the combined thickness of each film. This implies that the metal bottom layer is heated by both direct interaction with the laser radiation and heat conduction, the latter being dependent on the thermal conductivity, which is higher for Au than Pd. Figure 6 shows the SEM images of some representative samples before and after irradiation at three different pulse energies. The preirradiated samples show a surface morphology like a “bare” ZnO film [see Fig. 4(a)], confirming that the metal films are thin enough to not alter the morphology of the film below. Independently of the pulse energy, the irradiated samples show spherical nanoparticles that lie on a smooth surface. This means that one laser pulse is enough to produce the NPs, and that for the observed energies, the pulse also modifies the surface morphology of the ZnO film. The images also show that the presence of cracks on the surface of the ZnO film increases with the pulse energy and that they are more noticeable in the samples that contain Pd. This phenomenon can be explained by considering the simulated temperature in which at constant pulse energy, the samples containing Pd reach higher temperatures than those with a monometallic Au film. This temperature difference arises due to the higher evaporation temperature of palladium compared to gold. Consequently, even after the gold film has evaporated, the ZnO layer continues being heated by conduction in Pd-containing samples. Then, the more the Pd content, the higher the temperature reached. The cracks are formed because of the rapid heat and cool transient period, which produces melting and solidification of superficial layers of the ZnO film. This process induces a gradient of stress within the ZnO layer, producing the observed

![SEM images of three multilayered films: ZnO-Pd100 (top row), ZnO-Au50-Pd50 (middle row), and ZnO-Au100 (lower row). (a) As-grown samples and (b)–(d) after irradiation with one laser pulse, where numbers correspond to pulse energy in mJ.](image-url)
cracking. It should be mentioned that the ZnO film maintains the same crystallographic orientation after solidification (see Fig. S4 of supplementary material). 46

The bimetallic laser-produced nanoparticles consist of an alloy comprising both metals rather than being composed of distinct segregated phases. This can be verified by the x-ray diffraction spectra, which show only one peak corresponding to a compound phase for the bimetallic NPs instead of peaks of pure metal elements (see Fig. S4 of the supplementary material). 46 Formation of an alloy is expected since Au and Pd are miscible in a large range of temperatures including that predicted by the simulation. 42,43 In addition, previous works have reported that laser-induced dewetting of thin films produces Au–Pd alloy nanoparticles.

Figure 7 shows the mean diameter of the nanoparticles as a function of the deposition time of the Au film. The error bars correspond to the error of the algorithm to count the NPs from the SEM images.

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Figure 7 shows the mean diameter of the nanoparticles as a function of the deposition time of the Au film. The error bars correspond to the error of the algorithm to count the NPs from the SEM images.

In our case, the Pd films are rougher than Au films, thus affecting the size of the produced nanoparticles. The only point that shows a different tendency is that corresponding to a largest pulse energy (21 mJ) and made of pure gold. In that case, the mean diameter decreases probably because the energy is too high in such a way that there is considerable evaporation of gold.

4. CONCLUSION

We have exploited the laser-induced dewetting technique to efficiently produce Au–Pd bimetallic nanoparticles on a ZnO thin film with a single laser shot. This was achieved by nanosecond laser irradiation of three-layer film stacks deposited on glass, employing two different sequences: glass/ZnO/Pd/Au and glass/ZnO/Au/Pd. The threshold pulse energy, experimentally determined by means of transmitted light intensity ratio spectra, revealed an increase with the thickness of the Pd film in the stack. Interestingly, stacking order minimally influenced the threshold value, except in cases where the Au content exceeded 50%. Temperature simulations were used to predict the energy threshold required to melt monometallic Au or Pd film and, thus, to produce metal nanoparticles without inducing a phase change in the underlying ZnO film. Significantly, the threshold energy for producing Au nanoparticles was found to be lower than that for Pd NPs.

Given that the substrate is a thin film rather than a bulk material, heat diffusion and temperature gradients within this film directly impacted the maximum temperature reached within the thin metal films, as well as the time of liquid phase of the metal, consequently influencing the NPs size. It was found that an increased Pd content in the nanoparticles resulted in smaller nanoparticles.

This study demonstrates the potential of laser-induced dewetting for the fabrication of bimetallic metal alloy nanoparticles on semiconductor thin films. So, the implications of this extent to applications in the field of photocatalysis present exciting prospects for further research and technological advancements.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

C. Sánchez-Aké: Conceptualization (lead); Funding acquisition (lead); Investigation (lead); Project administration (lead); Supervision (lead); Writing – original draft (lead). J. A. Segura-Zavala: Investigation (equal); Methodology (lead); Writing – review & editing (equal). O. Depablos-Rivera: Investigation (equal); Methodology (equal). M. A. Martínez-Fuentes: Formal analysis (equal); Investigation
DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available within the article and its supplementary material and are available from the corresponding author upon reasonable request.

REFERENCES

See supplementary material online for a comprehensive overview of various aspects related to the temperature simulation. It includes detailed descriptions of the boundary conditions, mesh, and computational time used in the simulation. Additionally, it features a temperature-time profile and a plot of temperature as a function of depth (z), illustrating the temperature distribution across the film stack and the substrate. Furthermore, the supplementary material contains a comparison between the ZnO films before and after irradiation, showcasing any changes induced by the irradiation process. Finally, it includes x-ray diffraction spectra of the samples postirradiation, offering insights into the structural changes that occurred.