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# Effects of visible and synchrotron x-ray radiation on the growth of silver nanoplates on *n*-GaAs wafers: A comparative study

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A simple and effective approach has been developed to grow silver (Ag) nanoplates on *n*-type gallium arsenide (GaAs) wafers through a reaction between the wafers themselves and aqueous solutions of silver nitrate at room temperature [Sun and Wiederrecht, Small **3**, 1964 (2007)]. In this letter, the effect of green laser irradiation, which can efficiently excite the valence band of a GaAs substrate to form electron-hole pairs in the shallow surface region ($<3$ $\mu$m), on the growth of Ag nanoplates is studied. Illumination with the laser significantly depresses the growth of Ag nanoplates. In comparison, the influence of synchrotron x-rays, which can excite the deep core levels of elements and deeply penetrate ($>50$ $\mu$m) into GaAs lattices, on the growth of Ag nanoplates is also studied. The results indicate that the excited deep core levels can relax into electron-hole pairs in the band edges to induce similar effects to that of the green laser except that the larger area around the x-ray beam is affected to inhibit the growth of Ag nanoplates. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2924766]

The growth of metal nanostructures with controlled shapes on semiconductor substrates represents an interesting topic because of their unique optical properties and potential applications in photon related areas, such as photovoltaic cells,[1] photoelectrochemical splitting of water,[2] etc. The strategies generally adopted for creating metal nanostructures on semiconductor substrates include synthesis of metal nanostructures in solution via well-established approaches[3–7] followed by postdeposition (and/or assembly) of the as-synthesized nanostructures on the chosen semiconductor substrates.[8] Most of the solution-based synthetic approaches require surfactant molecules to direct the anisotropic growth of metal nanostructures as well as prevent them from aggregation. The use of surfactant molecules, however, complicates the reactions and contaminates the surfaces of the resultant metal nanostructures, leading to degradation of their performance in some applications.[9] Alternatively, a more straightforward method is to directly grow metal nanostructures on semiconductor substrates through reduction of aqueous solutions of pure metal precursors (e.g., $AgNO_3$ for Ag) by either the semiconductor substrates[10] or external electrical potential.[11] Recently, we have developed a simple and efficient approach to directly grow Ag nanoplates (with rough[12] and smooth surfaces[13]) on *n*-type GaAs wafers. Because GaAs is very sensitive to electromagnetic radiation, we compare the effects of illumination with a green laser and synchrotron x-rays on the growth of Ag nanoplates in this letter. The results also provide evidence to clarify the proposed growth mechanism in our previous studies.[12]

The experiments have been carried out as described elsewhere.[12,13] In a typical synthesis, a droplet ($\sim 15$ $\mu$l) of aqueous solution of $AgNO_3$ with concentration of $0.1M$ is delivered to the surface of a piece of *n*-type GaAs wafer [with dopant (Si) concentration of $\sim 1.0\times 10^{18}$ $cm^{-3}$ and a surface orientation of (100)], which is cleaned by soaking in a 2% hydrofluoric acid (HF) solution for 5 min. Once the $AgNO_3$ solution contacts the GaAs substrate, a green laser (wavelength of 532 nm, with a flux of $\sim 10^{18}$ photons/s, Coherent® Verdi-V10 laser source) is immediately turned on to illuminate a portion of the reaction area [Fig. 1(a)]. Figure 1(b) gives a scanning electron microscopy (SEM) image of the region [boxed by the black rectangle in Fig. 1(a)] includ-

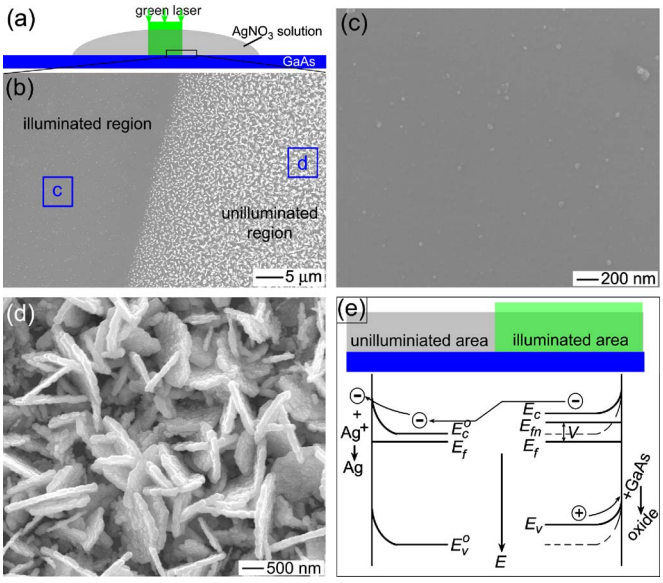


FIG. 1. (Color online) (a) Schematic illustration of the experimental setup for evaluating the effect of green laser irradiation on the growth of Ag nanostructures on an *n*-GaAs wafer. [(b)–(d)] SEM images of Ag nanostructures grown on a GaAs substrate after the reaction lasted 10 min. The frames of (c) and (d) correspond to the areas highlighted by the blue boxes labeled with corresponding letters in frame (b). (e) Diagram of the energy levels of the GaAs substrate in the illuminated and dark areas, showing the migration of electrons and holes as well as the corresponding reactions. The dashed curves in the right part of (e) represent the energy levels of conduction and valence bands under dark conditions.

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ing both illuminated and dark surfaces after the reaction has lasted 10 min at room temperature. The image clearly shows a stark contrast around the edge of the laser beam, i.e., only sparse small nanoparticles with sizes of 20–40 nm are formed in the center of the illuminated region [Fig. 1(c)], while the dark region is covered with dense nanoplates [Fig. 1(d)], which protrude out of the surface of the GaAs substrate. By considering the Gaussian distribution of power density of the laser beam, the existence of the sharp contrast in the image of Fig. 1(b) indicates that completely inhibiting the growth of Ag nanoplates requires illumination with power higher than a critical value. When illumination with power density is less than the critical value at the edge of the laser beam, the illumination cannot completely depress the growth of silver nanoplates. Instead, only a decrease in the density and size of the as-grown Ag nanoplates [which is indicated by the contrast gradient at the left side of the bright region in Fig. 1(b)] is observed. The nanoplates are made of pure Ag without any contamination from the GaAs substrate.[12] Similar to the structures obtained through reactions under dark conditions, the nanoplates shown in Fig. 1(d) also exhibit rough surfaces and thicknesses of 50–70 nm and edge lengths around 1 $\mu$m. The only difference is that the density of the Ag nanoplates shown in Fig. 1(d) is higher than that of nanoplates obtained under dark conditions. The increased density of nanoplates is ascribed to the enhanced density of surface electrons in the dark area of the GaAs substrate when the reaction area is partially exposed to the laser beam [Fig. 1(e)]. More electrons facilitate the formation of more nuclei and thus produce more nanoplates. The result is consistent with the Ag nanoplates grown on *n*-GaAs wafers with different doping levels under dark conditions, i.e., the density of Ag nanoplates increases with the dopant concentration, which determines the concentration of surface electrons. Charge separation and migration induced by the illumination is sketched in Fig. 1(e). When a *n*-type GaAs wafer is in contact with an electrolyte (i.e., aqueous $AgNO_3$ solution), the valence and conduction bands of the GaAs wafer bend upward in the space-charge region.[14] Illuminating the electrolyte-wetted area of the GaAs wafer with a green laser reduces the bending degree of the valence and conduction bands due to the photovoltage $V$. The electron quasi-Fermi level $E_{fn}$ under illumination is displaced from the equilibrium Fermi level $E_f$. The shift of energy levels in the illuminated area forces the photoinduced electrons in the conduction band of the illuminated GaAs to flow to the conduction band of the dark GaAs region though the bulk GaAs lattices, due to the energy difference of the conduction bands in different regions [Fig. 1(e)]. The enriched electrons in the dark region diffuse to the surface and subsequently reduce the $Ag^+$ to elemental Ag, which may contribute to the formation of nuclei. Although the surface electrons are possibly able to reduce $Ag^+$ to grow the nuclei into larger particles, further growth into nanoplates is dominated by a hole injection process. Each $Ag^+$ injects a hole into the lattice of GaAs though the Ag nuclei, resulting in the reduction of the $Ag^+$ into Ag and oxidation of GaAs into oxides.[12] On the other hand, the leftover holes in the valence band in the illuminated area cannot flow to the dark area because of the energy barrier. As a result, the holes diffuse to the illuminated surface to oxidize GaAs to form oxides,[15] preventing the deposition of Ag in the illuminated area. In addition, the holes may also oxidize the already deposited Ag particles (if possibly formed) to dissolve them. This mechanism is consistent with the typical behavior of a photoelectrochemical cell.[14,16] The correlation between the enhanced density of Ag nanoplates and the increased electrons in the dark regions agrees well with our previously proposed mechanism that the surface electrons of GaAs substrates account for the formation of the nuclei of the Ag nanoplates.[12]

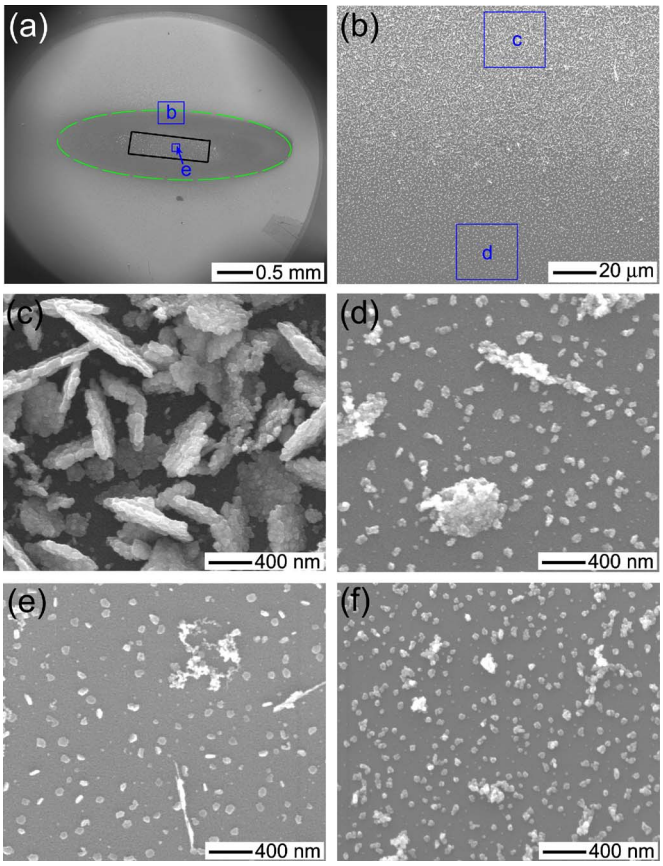


FIG. 2. (Color online) [(a)–(e)] SEM images of Ag nanostructures grown on an *n*-type GaAs wafer with a portion of the reaction area illuminated by an x-ray beam (marked by the black rectangle in frame a) after the reaction lasted ~11 min. The frames of (b)–(e) correspond to the areas highlighted by the blue boxes labeled with corresponding letters. (f) SEM image of Ag nanoparticles grown on an *n*-type GaAs wafer without x-ray illumination after the reaction lasted 30 s.

In comparison, illuminating an *n*-GaAs wafer with high-energy photons, e.g., synchrotron x-rays, which deeply penetrate GaAs lattices with a depth larger than 50 $\mu$m, leads to slightly different effects on the growth of Ag nanostructures. Figure 2(a) shows a SEM image of Ag nanostructures grown on a GaAs wafer when only the partial reaction area (marked by the black rectangle) is illuminated with x-rays. The experimental setup is similar to that shown in Fig. 1(a) except that x-ray irradiation is used. Experiments have been conducted at the bending magnet beamline 12-BM-B at the Advanced Photon Source, Argonne National Laboratory. A 12 KeV beam with flux of $3.8\times10^{10}$ photons/s modulated by a Si (111) monochromator is confined to 0.4 mm ($v$) $\times$0.4 mm ($h$) by slits and impinges on the GaAs wafer, which is tilted by ~10° against the horizontal plane. In a typical experiment, a drop of 0.1$M$ $AgNO_3$ solution is delivered onto the GaAs wafer followed immediately by an exposure to x-ray irradiation. Once the x-ray beam is blocked, the reaction is terminated after ~30 s (the delay is caused by opening the station hutch) by rinsing the wafer with plenty of

water. The SEM images [Figs. 2(a) and 2(b)] also show the existence of an apparent contrast between the areas outside and inside the dashed ellipse after the reaction has lasted ~11 min. Close observation of the bright region [marked with box c in Fig. 2(b)] shows the formation of dense Ag nanoplates [Fig. 1(c)], which are similar to the nanoplates formed on GaAs wafers under dark conditions. However, the side [marked with box d in Fig. 2(b)] and center [marked with box e in Fig. 2(a)] of the area inside the dashed ellipse [Fig. 2(a)] are covered with only small particles [Figs. 2(d) and 2(e)], which are similar (in terms of size) to the nanoparticles [Fig. 2(f)] formed on a GaAs wafer with a reaction time of 30 s and without x-ray illumination. It is, therefore, believable that the small nanoparticles formed inside the dashed ellipse are deposited after the x-rays are blocked. The result indicates that the x-rays generate a similar effect of blocking the formation of Ag nanoplates in the illuminated area. The difference is that the density of nanoparticles in Fig. 2(e) is much lower than that in Fig. 2(f) ($\sim 1.8\times 10^9$ versus $\sim 4.5\times 10^9$ $cm^{-2}$). The decreased density might be ascribed to the partial coverage of the oxide layer, which is formed upon x-ray irradiation on the illuminated surface of the GaAs substrate.

The comparable effects of the green laser and x-ray irradiation on the growth of Ag nanoplates on the *n*-GaAs wafers imply that the interaction between x-rays and *n*-GaAs also generates accumulated holes in the valence bands of GaAs in the illuminated areas. In general, x-ray irradiation excites deep core levels of elements followed by relaxation through Auger processes or secondary photon emission, which creates a cascade of secondary electrons, holes, and photons.[17] These secondary electrons and holes eventually thermalize to the band edges (i.e., electrons in the conduction bands and holes in the valence bands). The electrons and holes tend to migrate in the GaAs lattices and react with GaAs and $AgNO_3$, as shown in Fig. 1(e). Because x-rays can penetrate the GaAs lattices deeply (i.e., $>50$ $\mu$m), the holes generated in the valence band in the bulk lattices take a relatively long time to isotropically diffuse along all directions to the surface of the substrate to oxidize GaAs with assistance of water [Fig. 1(e)].[12] As a result, a broad region [i.e., the area outside the black rectangle and inside the ellipse in Fig. 2(a)] around the x-ray beam is influenced by the holes generated in the illuminated area, resulting in the absence of Ag nanoplates.

In summary, green laser irradiation and x-ray photons exhibit a similar effect on the growth of Ag nanoplates through the reaction between pure aqueous solution of 0.1*M* $AgNO_3$ and clean *n*-GaAs wafers. Irradiation of a portion of the reaction area inhibits the growth of Ag nanoplates in the illuminated regions (as well as the nearby regions). On the other hand, the density of nanoplates in the dark regions is increased by comparing with samples formed under complete darkness. This is ascribed to the enhancement of the concentration of surface electrons in the dark regions generated though photoinduced charge separation and migration. This provides direct evidence for our previously proposed mechanism that the surface electrons of GaAs substrates account for the formation of nuclei of Ag nanoplates.[12]

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