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Observation of two-dimensional holographic photovoltaic bright solitons in a photorefractive-photovoltaic crystal
Lateral photovoltaic effect observed in nano Au film covered two-dimensional colloidal crystals

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Periodic nanostructure, especially for nano-spheres’ structure, is one of the key issues in the current research, due to its anomalous transmission of light and obvious surface plasmon resonance. In this work, a type of anisotropic lateral photovoltaic effect is observed in the Au films covered two-dimensional colloidal crystals (CCs). This finding of lateral photovoltaic effect adds the functionality to the CCs system and will be useful in development of CCs-based devices.

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Photovoltaic field has recently witnessed an explosion of interest and progress in the study of periodic nanostructures, such as silicon-based carbon nanotubes,1 quantum dots.2,3 As one of the most attractive periodic nanostructures, the gold films covered two-dimensional colloidal crystals (CCs) have been widely investigated in the anomalous transmission of light4 due to its prominent characteristic of localized surface plasmon resonance (SPR)5 and have been proven to be the most charming platforms suitable for a broad range of biological and biomedical applications.6 It has been demonstrated that the radiative properties or spectroscopic signals from the molecules at the surface are dramatically enhanced by surface plasmon resonance in Au covered CCs.7 However, the photovoltaic properties in CCs-based nano-spheres’ structures, especially for lateral photovoltaic effect (LPE), have never been reported.

Different from the ordinary transverse photovoltaic effect which has been generally used in solar cells for many decades, LPE has been widely applied in position-sensitive detectors.8–12 It can be used to detect very small displacement, due to its linear change of lateral photovoltage (LPV) output with laser position. The LPE was first discovered by Schottky13 and later expanded upon by Wallmark in floating Ge p-n junctions in 1957,14 and then was boosted in many different systems,8–10 such as p-n junction, quantum dots, and metal-semiconductor structures. The main criterion to determine the performance of a position-sensitive detector is the sensitivity defined as the variation of LPV when the laser moves a unit distance. The reported sensitivities were mostly within the range of 1–20 mV/mm in the hydrogenated amorphous silicon and Schottky barrier structures systems11,12 found by Henry and Livingstone group.

In this Letter, we will show a large LPE with a sensitivity of 86 mV/mm observed on silicon-based Au covered CCs under the irradiation of 780 nm laser. This large sensitivity will ensure these CCs-based devices to work under high degree of reliability. It is expected that the SPR in Au covered CCs can hinder the excited electrons recombination with the holes. In the meanwhile, CCs may further modulate the photogenerated electrons diffusion by its size and direction. These two factors are crucial for obtaining a large LPE in CCs-based structures, which will be discussed later. Our results show that the combination of LPE with CCs presents great potential for applications, making it possible to add the functionalities to CCs-based optoelectronic devices, such as LPE type biosensors or other multi-functional photoelectric devices.

The substrates used in the experiments are n-type Si (111). The thickness of the Si wafers is around 0.3 mm and the resistivity is within the range of 50–80 Ω/cm at room temperature. The metallic microstructures were prepared by sputtering a thin gold layer onto a monolayer of dielectric microspheres self-assembled onto the substrates.15 The microspheres are silica beads purchased from Duke Scientific Corps and the diameter is 1.58 μm. The two-dimensional CCs were prepared by injecting an aqueous solution of colloidal dispersion with a suitable concentration into a channel that was formed from two parallel quartz slides separated by a U-shaped spacer. The quartz slides had been pretreated to render their surface hydrophilic by soaking in a solution of 30% hydrogen peroxide at 80°C for 30 min. After drying in air, CCs were grown within the channel under capillary force. The prepared CCs acted as a topographic pattern and the gold film was made by sputtering with an ion-beam coater (IBC Model 682, Gatan Corp.) on the top of the microspheres to the desired thickness at a rate of 1.2 Å/s−1 in a vacuum of 5×10−6 Torr. The two-dimensional arrays of metallic dielectric microspheres with a hemispherical metal coverage were fabricated. The thin gold film covered the microspheres and consisted of a hexagonally close-packed array of gold half-shells, whose diameters can be controlled easily by choosing colloidal microspheres with different sizes. Figure 1(a) shows the scanning electron microscopy image (SEM) of two-dimensional CCs.

In this paper, all samples were cut into 6 mm×12 mm rectangles and were scanned spatially with a laser (40 mW and 780 nm) focused on a roughly 50-μm diameter spot at

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the surface and without any spurious illumination (e.g., background light) reaching the samples, as shown in Figure 1(b), and both of the contacts (less than 1 mm in diameter) are simply made on the Au film by the method of pressing alloying indium (A and B, AB = L). As shown in Figure 1(c), comparing with the IV curves under no illumination, the conductivity of two-dimensional CCs with 5 nm gold film along 0° is very low. 0° is along the most close-packed direction for nano-spheres on the substrate and perpendicular to 90°. 45° is the bisector of two directions. As the direction goes from 0° to 90°, conductivity of the structure increases significantly. This is because the proportion of Au is the largest along 90° and become the smallest along 0°. According to Figures 1(c) and 1(d), we can see the thickness of Au plays a very important role in the conductive property. For the structure of Au(0 nm)/CCs/Si, IV curve shows obvious non-Ohmic behavior. And 5 nm, Au film is so thin that IV curves do not show Ohmic behavior which indicates that voltage has not been short circuited. As for the sample with 10 nm Au film, Ohmic behavior is observed from the IV curve, indicating the Au film plays a main role in the conduction.

With the laser irradiation on the surface of the structure as shown in Figure 1(b), we find an obvious lateral photovoltaic effect. The feature of LPE is quite similar with our previously reported LPE phenomenon. LPV keeps the largest when the incident radiation spot is closest to the electrodes and shows a monotonic linear decrease as the spot is scanned away from the contacts, becoming null at the midpoint between two contacts. The biggest sensitivity, we obtained in this structure is as much as 86 mV/mm with a fixed 0.4 mm contacts’ distance along 90° (see Figure 2(a)).

To gain additional insights into the LPE, we also investigated the distance-dependence. We can clearly find the sensitivity hugely depends on the distance between AB (defined as L) (see Figure 2(a)), i.e., as L increases from 0.4 mm to 1.25 mm, the LPV sensitivity can drop drastically from 86 mV/mm to 2.79 mV/mm. Different from the traditional flat film materials, this CCs-based structure has different orientations on sample surface. As an attempt, we choose to measure LPV along another two typical directions: 0° and 45°.
We find the sensitivity along 0° is much smaller than that of 90°, while the results from 45° fall in between, as shown in Figure 2(b) with \( L = 1.25 \text{ mm} \). The sensitivity along 90° is 2.79 mV/mm, which is almost 2 times larger than that of observed along 0° (1.65 mV/mm). So, the LPE is anisotropic in this CCs-based structure. However, testified by many repeated experiments, we found that the polarization of light has no effect on LPE. This is interesting that the anisotropic LPE may be used in angle-sensitive sensors.

In this report, the obtained LPE challenges our common sense that it should be difficult to observe in this CCs-based nano-spheres’ structure for oxide film thickness over 1000 nm, which is a high barrier for the excited electrons to tunnel. The reason why we can still observe a large LPE is that there is plenty of room (filled by Au) between adjacent CCs balls, as shown in Figure 1(a). Thus, this part of Au can be treated as a tunnel which bridges the Au surface and Si substrate. When a beam of photons impinge on the surface, photons with energy higher than the bandwidth can produce electron-hole pairs in the silicon at the illuminated area. Based on this mechanism illustrated by Figure 3(a), the excited electrons can transit from silicon onto Au surface through this Au tunnel and spread exponentially along the metal away from the illuminated spot. A charge distribution gradient is formed laterally between the zone of illumination and non-illumination on the surface, which can be described by

\[
D_m \frac{d^2N(r)}{dr^2} = \frac{N(r)}{\tau_m}, \quad N(r) = N(0) \exp \left( -\frac{r}{\lambda_m} \right),
\]

where \( \tau_m \) is the combination time of electrons and holes, \( N(0) \) is the initial electron number density, \( \lambda_m \) is the electron diffusion length in the metal surface, and \( D_m \) is the diffusion coefficient of metal. And \( \lambda_m = (D_m \tau_m)^{1/2} \). The number of collected carriers by the two ohmic contacts depends on their distances to the illuminated point. A lateral electric field can be formed in this way and lateral photovoltaic is generated. The sensitivity can be described by

\[
\text{Sensitivity} = \frac{d(LPV_m)}{dx} = \frac{d}{dx} K_m N(0) \left[ \exp \left( -\frac{|x- \lambda_m|}{2\lambda_m} \right) - \exp \left( -\frac{|x+ \lambda_m|}{2\lambda_m} \right) \right] \approx \frac{2K_m N(0)}{\lambda_m} \exp \left( -\frac{L/2}{\lambda_m} \right),
\]

where \( K_m \) is a proportional coefficient of metal side related to electron charge, mass, Fermi level,\(^{17}\) \( x \) is the laser position. When \( x \) satisfies \( |x| \ll \lambda_m \), LPV can be idealized as linear change with \( x \). Figure 3(b) shows the energy bands of Au/SiO\(_2\)/Si system.

The above involves the general analysis of LPE. This paper reveals a significant improvement on the LPE sensitivity (86 mV/mm) comparing with our previous work, where a maximum sensitivity of only 16.48 mV/mm in similar structure of Au/SiO\(_2\)/Si was obtained.\(^{18}\) The enhanced sensitivity is achieved as a result of a proper value of \( \lambda_m \) according to Formula (2). As shown in Figure 3(c), we can clearly see that the sensitivity, having a great bearing on the \( \lambda_m \), will decrease when \( \lambda_m \) is away from \( \lambda_{\text{opt}} \) (the optimum value).

The value of \( \lambda_m \) is determined by the structures’ parameters, such as the thickness of CCs and Au film. The structures corresponding to \( \lambda_1 \), \( \lambda_2 \), and \( \lambda_3 \) are labeled as (i), (ii), and (iii), respectively, and schematically marked on the sketch. It is very difficult for the excited electrons to tunnel through the thick oxide film in structure i, in which case \( \lambda_1 \) is almost zero. As a contrast, the excited electrons can tunnel onto the surface in structure ii with the mechanism we have explained.

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**FIG. 3.** (a) Schematic diffusion model of LPE in the structure. (b) Diagram of energy bands of metal-oxide-semiconductor structure (Au/SiO\(_2\)/Si). (c) The sketch of Formula (2) for different structures with different electron diffusion length \( \lambda_m \). \( \lambda_{\text{opt}} \) is the optimal value of \( \lambda_m \). (i) \( \lambda_1 \) represents for \( \lambda_m \) in control sample Au(5 nm)/SiO\(_2\)(1.58 \text{ nm})/Si, (ii) \( \lambda_2 \) represents for \( \lambda_m \) in control sample Au films covered two-dimensional CCs, and (iii) \( \lambda_3 \) represents for \( \lambda_m \) in control sample Au(40 nm)/SiO\(_2\)(1.2 nm)/Si as discussed in Ref. 18.
above, leading to $\lambda_2 > \lambda_1$. In structure iii, 1.2 nm SiO$_2$ film is transparent to electrons at room temperature.\textsuperscript{19} The excited electrons will tunnel through the oxide layer into the metallic film. Meanwhile, 40 nm Au film is much thicker for electrons diffusion because of a very small resistance. Thus, $\lambda_3$ is much larger and we get that $\lambda_1 < \lambda_2 \ll \lambda_3$ as shown in Figure 3(c). So it can be understood why Au film covered CCs sees a remarkable LPE sensitivity.

In fact, our work may imply a way to improve LPE. We can obtain enhanced LPE with $\lambda_{opt}$ through optimizing $\tau_m$ from both sides of the structures’ parameters and laser wavelength, since $\lambda_m$ is defined as $\lambda_m=(D_m\tau_m)^{1/2}$. There are two factors contributing to a more suitable $\tau_m$ in structure ii. The first one is periodic characteristic of CCs that can effectively dilute the recombination during the diffusion of the excited electrons. As shown in Figure 3(a), the recombination probability varies periodically and reaches maximum between adjacent CCs balls (filled by Au), which is remarkably different from the equally distributed case in flat nano-film structure. The other factor is the localized SPR, the most prominent feature for CCs system. For our samples, the anomalous transmission of light and SPR have been thoroughly studied in near infrared region.\textsuperscript{5} We utilize a laser 780 nm in wavelength, which is very close to the theoretically calculated transmission resonance wavelength of 789 nm, to produce hole-electron pairs at illuminated area in the silicon (with a forbidden energy bandwidth of 1.12 eV). When SPR is stimulated by a laser in the structure, electron resonance can work as a trap at the laser illuminated spot to hold back the re-combination of excited electrons with holes. Further investigations are needed to verify whether there is any intrinsic connection between LPE and SPR.

As to the anisotropic features of LPE, we think it can be attributed to the difference of $\lambda_m$ along different directions. The proportion of Au in the structure is different along different directions, leading to different resistivities, i.e., different $D_m$ (note $D_m$ is inversely proportional to resistivity). This is in agreement with the measurements of IV curves in Figure 1(c), which shows results of different resistivity in three directions. For instance, along 90°, Au has a longest diffusion length due to the largest Au composition, resulting in a larger LPE. According to Figure 3(c), the sensitivity increases monotonically with $\lambda_m$ that falls in between zero and $\lambda_{opt}$. And investigations of anisotropic features may be applied to optimize the samples’ parameters.

In conclusion, a large lateral photovoltaic effect with a high sensitivity of 86 mV/mm is achieved in the Au films on two-dimensional CCs. This result adds the functionality to the CCs system and may stimulate both theoretical and experimental efforts in these two-dimensional metal-dielectric microstructures, especially to exploit their potential applications in the near-infrared spectral region.

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