Photo-induced Voltage in Nano-porous Gold Thin Film

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We report an experimental study of generation of photo-induced voltage in nano-porous gold (NPG) thin film under the radiation of obliquely incident nanosecond laser light in visible regions. For s-polarized light, negative photo-induced voltage is observed along the incident plane for positive incident angles, suggesting momentum transfer from photon to free electrons in NPG. For p-polarized light, however, positive voltage is observed for wavelength longer than 510nm, while it turns to negative for shorter wavelengths. As for the direction perpendicular to the incident plane, photo-induced voltage is observed for oblique incident circularly polarized light with sign depending on the sense of polarization rotation. Similarly for ±45° linearly polarized light the voltage sign changes depending on the polarization sign. The polarization dependence of transverse voltage is explained in terms of symmetry of configuration and that of microscopically random but macroscopically isotropic NPG.

Keywords: Nano-porous gold, photo-induced voltage, laser, polarization

I. INTRODUCTION

It is known that photo-induced voltage is generated in conducting thin film during the interaction of laser pulses and the simplest description for this observed voltage is that when structure is radiated by light, light can push electrons through Lorentz force due to its electric and magnetic fields. The force on electrons can be detected as a voltage in the structure. This force can be estimated using momentum conservation, that is, momentum from photons transfers to the free carriers of the material and this effect manifests itself as a pulsed voltage [1, 2]. This phenomenon has been investigated by other groups in various materials and explained in terms of photon drag effect, optical rectification, photogalvanic and etc.[2–5].

Photon drag effect is significant in semiconductors [6] and very small in bulk metals[5]. In principle, photon drag effect is expected for surface of metals like gold. In metals, this effect can be observed as the surface current that uniquely depend on the incidence angle and the polarization of the exciting light[4]. The photon drag effect induced current in metals without surface plasmon resonance has been described using equation of motion for the electrons within a hydrodynamic model[7]. Vengurlekar and Ishihara have reported enhanced photon drag effect in a thin gold film when the incident light excited surface plasmon. They showed that the observed photovoltage depends on the incidence angle and polarization of light [8].

In systems without inversion symmetry, light can induce DC polarization in the structure that is second order in terms of electric field. This term is referred to as optical rectification and is responsible for the voltage. Hatano et al. measured optical rectification due to photonic scale asymmetry. When laser beam is normally incident to the sample, the photovoltage is observed only for photonic crystal with asymmetric unit cells [3]. Ishihara et al. measured optical rectification in a thin metallic film with square array of periodic circular holes. The transverse voltage induced by obliquely incident circularly polarized light was explained in terms of optical rectification [9].

In this paper we report for the first time photo-induced voltage in Nano-Porous Gold (NPG) films, which is generated by corrosion of an alloy of gold and less noble material such as silver. NPG has attracted attention because of simple preparation techniques to fabricate nanostructures compare to other methods such as Electron Beam (EB) or Fast Ion Beam (FIB) lithography. It is used in the field of sensors, actuators, optics, and many more areas [10].

Because of these nano-size pores in the structure, surface plasmon like excitation is expected upon light irradiation. Conductive character allows detection of photo-induced voltage in NPG. We have studied polarity and amplitude of the pulsed response voltage of NPG and show that they depend on the incidence angle, type of polarization and wavelength of incident light.

II. EXPERIMENTAL

NPG thin film can be generated by dealloying of some suitable alloys of gold like AuAg, AuCu and AuNi. In this process, the less noble component is removed and the more noble material in the alloy, here gold, remains and forms an interconnected nanostructure of pores and gold. We dissolved silver from alloy of AgAu by exposure of a 50% - 50% alloy to 65% concentrate HNO3 for 30 minutes. Then it was removed from acid and rinsed in distilled water to remove the residual acid. After rinsing, the film was transferred onto the center of a 15 × 15 mm glass substrate with evaporated Au electrodes. Then the film was trimmed with a focused laser into of dimensions 3 × 3 mm. Typical thickness of the NPG films was about 100 nm.

Each sample was provided with two parallel electrodes. For connecting two electrodes to the NPG film for measuring photo-induced voltage, we used vacuum evaporator to make a 50 nm layer of gold on the glass sub-
substrate with a gap for attaching NPG film. Before that, a 50 nm thick intermediate layer of Cr was evaporated on the substrate for better adhesion. Then NPG was directly mounted in the gap, and pieces of copper tapes were connected on the evaporated gold to make connection between film and electrodes. Finally, two leads as electrodes were soldered to the copper tapes. After the attachment of the electrodes, the substrate was fixed on a 20 × 20 mm printed circuit board (PCB). The typical ohmic resistance of the films was 12 Ω.

In our experiment, we employed two configurations; longitudinal (the electrodes were oriented perpendicular to the incidence plane and the voltage along x axis was measured) and transverse (the electrodes were oriented parallel to this plane and the voltage along y axis was measured) (see Fig. 2). The observed photo-induced voltages; longitudinal photo-induced voltage (LPIV) and transverse photo-induced voltage (TPIV), were measured for different types of polarization (circular polarized light and ±45° linear polarized light for transverse configuration. Circular polarized light, s- polarized light and p- polarized light for longitudinal configuration). Positive incident angle is shown by the arrow in Fig. 2.

When free electrons are dragged toward positive electrode with the projection of k vector in that direction (direction of the photo-induced voltage is toward the positive electrode of the sample), we have a negative signal on the monitor of the oscilloscope. Peak of this negative signal is measured as a negative voltage in angle resolved and wavelength resolved voltages and in the graph of data it is shown with a negative voltage.

Figure 3 shows a schematic diagram of the experimental setup. Light from an optical parametric oscillator (OPO) was pumped by tripled YAG:Nd laser and produced both idler wavelengths (light with 710-2300 nm) and signal wavelengths (light with 450-700 nm). We used signal wavelengths between 450 to 600 nm for wavelengths resolved measurement keeping the light intensity constant with a computer controlled half-wave plate and a polarizer (Glan-Taylor prism).

The laser pulse width and repetition rate were 7 ns and 10 Hz, respectively. The polarization of light was controlled with an achromatic half wave plate or quarter wave plate from Thorlabs. The beam size was chosen so that it covers the sample at the normal incidence. For keeping intensity of incident light constant (4 MW/cm² at normal incidence for all wavelengths) we used a half wave plate on a rotational stage between OPO and a Glan-Taylor prism in the setup.

A sample was mounted on a rotational stage, so that we can change incidence angle of the light for measuring angle resolved photo-induced voltage. We measured peak of photo-induced voltage for different configurations with a digital oscilloscope (Tektronix TDS3012B with 50Ω input impedance and pass band of 100MHz) which is triggered by Q-switch of the laser. An amplifier with a gain of 125 was used before feeding induced voltage to the oscilloscope. For reducing pulse to pulse fluctuations in the
photoinduced signal, they were averaged for 32 pulses.

III. EXPERIMENTAL RESULTS

A. Transmission Spectra

In order to characterize our sample, we first compared transmission spectrum of NPG film with an evaporated gold film. As is shown in Fig. 4, transmission peak of the NPG film locates significantly lower than that of the evaporated gold film, which is due to the lower effective electron density and responsible for the copper-like color of NPG.

B. Transverse Voltage

We measured photo-induced voltage along y axis of the NPG film in transverse configuration with circularly polarized and ±45° linear polarized light.

As we see in Fig. 2 NPG film is in the xy plane and incident laser beam is in the zx plane. In this condition with circular polarized light, when electric field of the light rotates clockwise in the xy plane as is looked toward the propagation direction, we refer this polarization as Right Circular Polarization (RCP) and when it rotates anticlockwise, we define it as Left Circular Polarization (LCP).

Figure 5 presents the experimental dependence of the photo-induced voltage on the incidence angle, \( \theta \), for transverse configuration with RCP and LCP.

For the same incidence angle, sign of the voltage for RCP is opposite of voltage for LCP. So, polarity of the voltage changes as the sense of polarization rotation changes from RCP to LCP. By increasing incidence angle from zero to larger angles, voltage increases for both negative and positive directions. At about \( \theta = +50° \), for RCP there is a maximum positive voltage. For LCP, we have a maximum negative voltage at this angle. For angles larger than \( \theta = +50° \) voltage decreases and at \( \theta = ±85° \) voltage is almost zero. So, angle dependency of amplitude of the voltage can be proportional to \( \sin(2\theta) \) for both RCP and LCP, which is proportional to the amount of photon momentum along the sample multiplied with photon flux.

Figure 6 shows dependence of the photo-induced voltage on the wavelength, \( \lambda \), for transverse configuration with RCP and LCP light at fixed incidence angle, \( \theta = +50° \). As it is clear from Fig. 6, intensity of induced voltage between 450 to 520 nm is almost the same but for longer wavelengths it gradually increases.

Sign of the TPIV does not change by changing wavelength in this wavelength range, for RCP it is always positive and for LCP always negative. For producing ±45° linear polarized light, an achromatic quarter wave plate was replaced with the half wave plate in the setup. For both case the Glan-Tayler prism was adjusted for p- po-
as we saw above (intensity of induced voltage between 450 to 520 nm is almost the same but for larger wavelengths it gradually increases). Sign of the TPIV does not change by changing wavelength in this wavelength range (for +45° it is always positive and for −45° always negative).

C. Longitudinal voltage

We measured photoinduced voltage along x axis of the film in longitudinal configuration with circularly polarized and s- and p- polarized light. By rotating sample +90° around z axis, configuration of the film changes from transverse to longitudinal. For producing p- and s- polarized light with 550 nm, a Glan-Taylor prism and half wave plate were used in the setup.

Angle resolved photo-induced voltage at the wavelength of 550 nm in longitudinal configuration with s- and p- polarized light are shown in Fig.9. For s- polarized light it follows \( \sin(2\theta) \) dependence and the sign is negative for positive angles. It is reasonable as electron has negative charge, which is pushed by light momentum. At about \( \theta = +50° \), for s- polarization there is a maximum negative voltage. Surprisingly for p-polarization, photo-induced voltage is almost zero up to \( \theta = +30° \) and becomes positive for larger positive incident angle. At about \( \theta = +65° \), there is a maximum positive voltage.

Wavelength resolved photo-induced voltage on the wavelength in longitudinal configuration with p- and s- polarized light are shown in Fig.10. For s- polarization, it is always negative for positive incident angle. On the other hand, we found that for p- polarization the sign of the voltage changes depending on the wavelength, from 450 to 510 nm this voltage is negative, while from 510 to 600 nm it is positive.

The reason for this tendency needs more investigation, but it may be related to the fact that the effective dielectric constant of NPG turns to positive for shorter wavelengths. Then surface plasmon polariton like excitation is responsible for observed positive voltage for p-polarization at longer wavelengths.

Angle dependence of photo-induced voltage in longitudinal configuration with RCP and LCP are shown in Fig.11. Sign and intensity of the voltage for RCP is the same with LCP. So, voltage does not change as the sense of circular polarization changes from RCP to LCP. At about \( \theta = +70° \), for both RCP and LCP there is maximum positive voltage. At \( \theta = -70° \), there is maximum negative voltage. For angles larger than \( \theta = +70° \) voltage decreases and at \( \theta = ±85° \) there is no voltage. It seems this voltage is made by adding s- and p- polarization together. Wavelength dependence photo-induced voltage in longitudinal configuration with RCP and LCP are shown in Fig.12 for \( \theta = +50° \). This data suggests that wavelength dependence for circular-polarized light excitation is the average of curves for s- and p-polarized light in Fig.10, as is consistent with the angle dependence in Fig.9 and

Figure 7 shows experimental dependence of the photo-induced voltage on the angle of incidence for transverse configuration with ±45° linear polarized light.

Shape of the signal resembles shape of laser pulses and is proportional to power of the applied light. By increasing incidence angle from zero to larger angles, voltage increases for both negative and positive directions. Sign of the voltage for +45° linear polarization is opposite of the −45° linear polarization. So, polarity of the voltage changes as the sense of polarization changes from positive to negative.

At about \( \theta = +50° \), for +45° linear polarization, there is a maximum positive voltage. For −45°, we have a maximum negative voltage at this angle. For angles larger than \( \theta = +50° \) voltage decreases and at \( \theta = ±85° \) voltage vanishes.

Figure 8 shows dependency of the photo-induced voltage on the wavelength for transverse configuration with ±45° linear polarized light. It shows wavelength dependence of voltage is similar to that for circular polarization.
D. Discussion

As we saw all measurements, signals and laser pulses are nanosecond signals and amplitudes of the signals are proportional to a characteristic law, $\sin(2\theta)$, for all TPIV and s-polarization case for LPIV, which is proportional to photon momentum and photon flux.

There are no TPIV for s- or p- polarized light. Intensity of signals are also proportional to the power of the laser beam. All these observed are characteristic features of the optical rectification observed in previous works with noncentrosymmetric crystals[2, 11], but in contrast to them our thin film is a random nanostructure. It suggests that even though microscopically NPG is random, it can keep phase and polarization information of light. The argument of polarization dependence based on the unit cell symmetry [3] does not apply here and we need more general explanation.

In order to explain the polarization dependence of photo-induced voltage in NPG, let us consider the mirror transformation ($y \leftrightarrow -y$) of the whole system including incident beam with respect to the incident $xz$-plane as Fig. 13 for TPIV and Fig. 14 for LPIV. First, we introduce the response function of photo-induced voltage as

$$V(E) = \begin{pmatrix} V_x(E) \\ V_y(E) \end{pmatrix}$$

for the case of incident electromagnetic wave with electric field $E$. Through the transformation depicted in Figs. 13 and 14, we can easily see that the following relation exactly holds between the response of the original system and that of its mirror image, $V^m$,

$$V^m(E^m) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} V(E) = \begin{pmatrix} V_x(E) \\ -V_y(E) \end{pmatrix}$$

where $E^m$ is the mirror image of $E$. On the other hand,
FIG. 13. Mirrored transverse configuration

when a NPG thin film is too random to be macroscopically distinguished from its mirror image, the relation

\[ V(E) \cong V^m(E) \]

should be approximately satisfied, and leads to the phenomenological consequence.

\[
\begin{pmatrix}
V_x(E^m) \\
V_y(E^m)
\end{pmatrix} \cong 
\begin{pmatrix}
V_x(E) \\
-V_y(E)
\end{pmatrix}
\]

This argument explains the polarity with respect to the polarization state of incident beam for every measurement in Figs. 5, 7, 9, and 11.

Next, bringing in a hypothesis, we would like to push forward the above discussion to predict photo-induced signals for generic polarization through the data in hand. Our proposal for the hypothesis is summarized as follows,

\[
V(E) = \frac{1}{2} \left[ \Re \left( z_p z_s \right) V_d(|E|, \theta) - \Im \left( z_p z_s \right) V_c(|E|, \theta) \right]
\]

where \( E = |E|(z_p e_p + z_s e_s) \), and \( z_p \) and \( z_s \) are complex coefficients satisfying \(|z|^2 = |z_p|^2 + |z_s|^2 = 1\) and representing the polarization state of incident beam, \( e_{p(s)} \) is the polarization vector of \( p(s) \)-polarization, and \( \theta \) is the angle of incidence. By appropriately choosing the functions \( V_{p(s,c,d)} \), we can make this form of response consistent with all the data in hand. Reversely, the consistency of this hypothesis with the data in Fig. 9 fixes \( V_p \) and \( V_s \), and the consistency with the data in Figs. 5 and 7 fixes \( V_c \) and \( V_d \) respectively. The results in Figs. 5 and 7 also suggest \( V_c \cong V_d \) at least for the case of \( \lambda = 550 \) nm.

Further analysis on the verification and validation of the hypothesis will be reported elsewhere.

E. Conclusions

We have experimentally investigated angle and wavelength dependence of TPIV and LPIV in NPG thin film. The \( \sin(2\theta) \) dependence observed in TPIV for circular polarized light and LPIV for \( s \)-polarized light suggests photon momentum transfer to the sample. On the other hand, LPIV shows extraordinary response when the excitation involves \( p \)-polarization for wavelength longer than 510 nm: The photo-induced voltage is positive for positive incident angle, which cannot be explained by simple momentum transfer argument. The angle dependence does not follow \( \sin(2\theta) \) dependence and exhibits maximum at higher angle of 60° in this case. In order to connect this behavior to surface plasmon like excitation, measurement of permittivity in NPG is in progress.

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