Surface-plasmon-enhanced photoelectron emission from nanostructure-covered periodic grooves on metals

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In this paper, we find that the resonant angle of surface plasmons (SPs) excited on a unique type of nanostructure-covered laser-induced periodic surface structure (NC-LIPSS) on platinum can be significantly different from the calculated value based on regular periodic grooves. We believe that this SP resonant angle shift is caused by an increase in the real part of the effective refractive index at the air-metal interface. We also find that the excitation of SPs can significantly enhance photoelectron emission on NC-LIPSSs.

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I. INTRODUCTION

Photoelectron emission from metals induced by external light has been studied extensively for more than one century.[1–10] With the advent of ultrashort high-intensity laser pulses, new phenomena in photoelectron emission have been observed, such as multiphoton photoemission and above-threshold photoemission.[3–6] Recently, studies also showed that multiphoton photoelectron emission can be significantly enhanced by surface plasmons (SPs), which is the collective electron excitation on a metal surface through grating coupling or attenuated total reflection coupling.[7–9] Although it has been suggested that the field strength of the surface electromagnetic wave[8] and the effective nonlinear low-frequency force[9] resulting from SPs may play a role in the enhanced photoemission, the mechanisms of SP effects on photoelectron emission are still unclear. Since the lifetime of SPs is on the order of femtosecond (fs) laser pulse duration,[9] the enhancement of photoelectron emission due to SPs may induce ultrashort high brightness electron pulses. Therefore, photoemission assisted by SPs can have many important applications, such as being used for ultrashort x-ray sources and laser cathodes for free-electron laser.[10,11]

Recently, we found a unique type of surface structure, i.e., nanostructure-covered laser-induced periodic surface structures (NC-LIPSSs), on metals following irradiation of high-intensity fs laser pulse.[12] We also found that NC-LIPSSs can significantly change the optical properties of the metal surfaces.[12] NC-LIPSSs can couple optical pulse energy into propagating SPs. Furthermore, the nanostructures on LIPSSs can change the dispersion relationship of the SP modes.[13] Therefore, the unique NC-LIPSSs may have some interesting effects on SP excitation and SP-induced photoelectron emission.

In this work, we study photoelectron emission from a platinum (Pt) surface covered with NC-LIPSSs by exciting SPs. We find that the resonant angle for SP excitation on NC-LIPSSs is significantly different from the calculated value based on regular periodic grooves. We believe that this angle shift is due to the increase in the real part of the effective refractive index of the Pt surface covered by NC-LIPSSs.[12] We also find that photoelectron emission current from the NC-LIPSS surface is greatly enhanced.

II. EXPERIMENTAL SETUP

Our experiment employs two amplified Ti:sapphire fs laser systems, one high-power system, and one high-repetition-rate system. The high-power fs laser system generates 65 fs pulses of an energy of 1 mJ/pulse at 800 nm with a 1 kHz repetition rate, while our high-repetition-rate laser system generates 60 fs pulses of an energy of 4 μJ/pulse at 810 nm with a 273 kHz repetition rate. We first use the high-power fs laser system to produce a Pt sample covered with NC-LIPSSs, as described in detail in Ref. 12. Surface

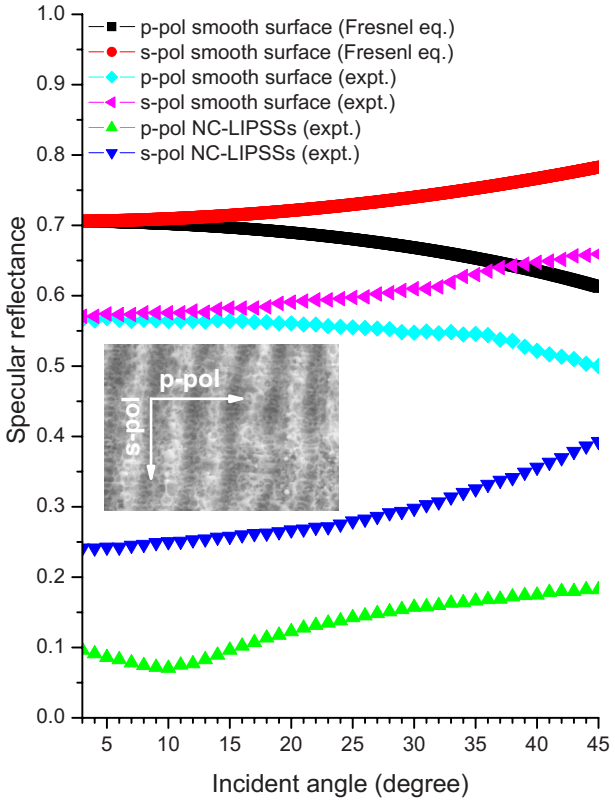

FIG. 1. (Color online) Dependence of specular reflectance on the incident angle for *p*- and *s*-polarized lights on both the NC-LIPSS and smooth Pt surfaces at 810 nm. For smooth surfaces, the calculated angular-dependent reflectances based on the Fresnel equations are also plotted.

morphology of NC-LIPSSs is characterized using a scanning electron microscope (SEM), and a typical image of NC-LIPSS is shown in the inset of Fig. 1. The period of NC-LIPSSs on Pt is measured to be about 530 nm, in consistence with the previous report.[12] To compare photoelectron emission process from a surface covered with NC-LIPSSs to a smooth surface, we also prepare a smooth Pt sample by mechanically polishing it with 0.1-μm-grade aluminum oxide powder. Subsequently, we perform all the measurements with our high-repetition-rate system. To find the resonant SP coupling angle, we perform an incident-angle-dependent reflectance measurement with both *p*- and *s*-polarized light. In this measurement, specularly reflected light is collected and measured by a power meter. The laser beam is slightly focused onto the NC-LIPSS and smooth samples in an intensity range of $(0.5-2.7)\times 10^{10}$ W/cm^2 that is below the damage threshold of the NC-LIPSS surface. The photoelectron current measurements are performed inside a vacuum chamber. To measure photoelectron current induced by fs laser pulse excitation, a metal wire is mounted as an anode at a distance of 1 mm away from the sample surface, and we apply a voltage of 1500 V to extract the emitted electrons. The biased metal wire is also used to reduce the space-charge effect that may suppress photoelectron emission from the sample. A picoammeter is used to measure the photoelectron currents from the NC-LIPSS Pt surface. The photoelectron current is sampled over a time interval of 500 μs, and the final signal is an average of 100 of these time intervals. Before data collection, we first irradiate the sample with a moderate intensity to eliminate possible contaminations on the surface.[14]

III. RESULTS AND DISCUSSIONS

To study photoelectron emission with SP excitation, we first need to determine the resonance angle to excite SPs on a NC-LIPSS surface. To do so, we vary the laser beam incident angle and record the reflectance of the specularly reflected beam at both *p* and *s* polarizations. As shown in Fig. 1, the angular-dependent reflectance from the smooth surface follows the predictions of the Fresnel formula, where the *p*- and *s*-polarized light reflectances diverge from normal incidence, except lower by an offset of about 0.13 that is mainly due to nonspecular scattering losses because of imperfections of the mechanically polished surface.[15] For the NC-LIPSS surface, the sample is mounted so that the groove structures are parallel to the *s* polarization and perpendicular to the *p* polarization. First of all, we notice that, unlike the smooth surface, the reflectance from the *p*- and *s*-polarized lights does not converge at normal incidence for the NC-LIPSS surface. At normal incidence, *p* and *s* polarizations are not distinguishable, and therefore, any randomly oriented structures, such as nanostructures, should not contribute to the difference in reflection at normal incidence. Furthermore, diffraction does not play a role at normal incidence in our study since the period of NC-LIPSSs is less than the incident light wavelength. Therefore, additional channels of energy coupling have to be carefully considered. We note that the *k* vector of NC-LIPSSs is parallel to the surface component of the incident *p* polarization, and this will allow light coupling in the form of SPs onto the NC-LIPSS surface. Therefore, we see a significant difference in reflectance between the *p*- and *s*-polarized lights at normal incidence for NC-LIPSSs. At off-normal incidence, diffraction may play a role for the difference in the specular reflectance between *p* and *s* polarizations in addition to the intrinsic difference from off-normal incidence. However, different polarizations should only affect the efficiency of the diffraction process. If diffraction was to play a role, we would expect to see that both *p* and *s* polarizations follow a similar pattern in angular dependence. Instead, however, we observe a minimum reflectance only for *p*-polarized light but not from *s*-polarized light, indicating that diffraction is not the cause for the observed minimum reflectance angle. Consequently, we believe this minimum reflectance angle is due to resonant coupling of SPs.

In fact, the minimum reflectance angle can be deduced from the period *d* of NC-LIPSSs measured in our experiments. To provide the additional momentum to excite SPs on a NC-LIPSS surface, the period *d* of NC-LIPSSs has to relate to the SP resonant angle θ following the condition below[16]

$$d = \lambda/(\eta \mp \sin\theta), \tag{1}$$

where $\eta=\mathrm{Re}[\varepsilon/(\varepsilon+1)]^{1/2}$ is the real part of the effective refractive index of the air-metal interface for SPs, ε is the dielectric function of the metal, θ is the SP resonant angle, and λ is the wavelength of the incident light. For an optically flat interface between air and Pt, η is 1.0075 at $\lambda=810$ nm.[17] As pointed out earlier, the groove period *d* is 530 nm, and if we use $\eta=1.0075$ and $\lambda=810$ nm, we will obtain $\theta\approx 31°$ from Eq. (1). However, in our measurements, the minimum reflectance angle for *p*-polarized light is 11°, which is significantly different from the calculated angle of 31° above. Therefore, additional mechanisms must be carefully considered.

Based on the argument above, our experimentally observed SP resonant angle of 11° corresponds to η increasing from 1.0075 to 1.338 or 1.718 depending on the sign used in Eq. (1). In one of our previous reports,[12] we found that the period of NC-LIPSSs continuously decreases with increasing number of pulses at normal incidence. This indicates that η increases monotonically with the number of pulses and the value of η will have to increase from 1.0074 to 1.338 given that Eq. (1) reduces to $d=\lambda/\eta$ at normal incidence.[12] To explain this increase in η, we note that the table values for ε_1 and ε_2 for Pt are obtained from a smooth surface at room temperature, and the table values may not be suitable when the metals are heated by high-intensity fs laser pulses and covered with nanostructures. It is known that surface roughness causes an increase in the modulus of SP wave vector,[18] and this will correspond to an increase in the real part of the effective refractive index. According to Eq. (1), η increasing from 1.0074 to 1.338 will cause the SP resonant angle to reduce to 11°, and this change of η will also reduce the NC-LIPSS period to the observed value of about 530 nm as discussed previously in Ref. 12. Both our experiment here

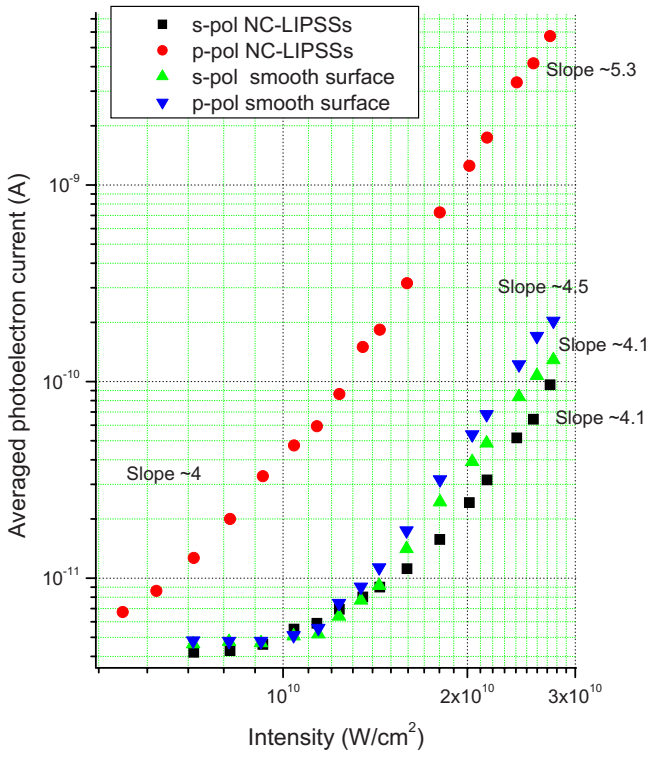

FIG. 2. (Color online) The averaged photoelectron current versus the laser intensity with p and s polarizations on both the NC-LIPSS and smooth Pt surfaces with an incident angle of 11°.

and our previous observation in Ref. 12 show that η indeed increases from 1.0074 to 1.338 due to surface nanostructures and high-intensity laser irradiation.

It is also worth noting that the shape of SP resonant peak of NC-LIPSS is significantly different from regular metallic groove structures, which are usually much sharper and deeper. This angular broadening of SP excitation cannot be explained simply by considering the spectral bandwidth [$\Delta\lambda$ full width at half maximum (FWHM)$=35$ nm] of our fs laser pulse. In fact, nanostructures on NC-LIPSSs consist of a large range of k vectors that will contribute to and significantly broaden the overall k vector of NC-LIPSSs. The broadened k vector of NC-LIPSSs may significantly relax the phase matching conditions for SP excitation and broaden its angular coupling range, leading to an enhanced photoelectron emission over a broad range of incident angles.

Once we determine the SP resonant angle on NC-LIPSSs, we study photoelectron emission with SP excitation. Photoelectron emission yields from Pt are measured as a function of laser intensity for both p and s polarizations, as shown in Fig. 2. For Pt, four-photon energy is required to overcome the work function of 5.64 eV to emit a single electron based on Einstein's photoelectric equation.[1,19] To understand photoelectron emission shown in Fig. 2, we also consider an additional factor that depends on the incident light intensity in multiphoton photoemission. For N-photon photoemission process by ultrashort laser pulse irradiation, the relationship between the photoelectron current density and the intensity of laser light is given by $J=\Sigma_{N=0}^{\infty}J_{\beta(N)}=\Sigma_{N=0}^{\infty}\sigma_N I^N(I/I_c)^{\beta(N)}$,[11] where σ_N is the cross section of the pure N-photon photoemission process for laser pulses much longer than electron-phonon relaxation time, I_c is the intensity threshold when photoelectron emission yields deviate from the pure N-photon process, and I is the laser intensity. $\beta(N)$ is a positive value for $I>I_c$ and zero for $I\leq I_c$.[11] Therefore, for $I\leq I_c$, the slope of the log-log plot of photoelectron current versus laser intensity shows the order of multiphoton process, but for $I>I_c$, the slope is higher than the order of multiphoton process due to nonequilibrium between hot electrons and a cold lattice.[11]

First of all, we can see from Fig. 2 that the photoelectron emission yield induced by p-polarized light from NC-LIPSSs is much higher than those induced by s-polarized light from NC-LIPSSs and by both p- and s-polarized lights from a smooth Pt surface. We note that p polarization is most efficient in exciting SPs, and the excitation of SPs can enhance the electric field on NC-LIPSSs for p polarization; we believe that this leads to the overall enhanced photoelectron yield. For photoelectron emission yield induced by the p-polarized light from NC-LIPSSs, a slope starts from nearly 4 over an intensity range of 5–15 GW/cm^2 but starts to increase for intensity above 15 GW/cm^2 and finally reaches 5.3 at 27 GW/cm^2. For intensities lower than 15 GW/cm^2, pure four-photon process is the dominant process, and other processes, such as nonequilibrium enhanced process, thermally assisted, or thermionic photoemission, seem to be negligible. However, for intensities higher than 15 GW/cm^2, the effect of nonequilibrium heating of hot electrons by fs pulses seems to be strong enough and enhances the slope of the total photoelectron current to above 4. Thermally assisted photoemission current can also contribute to the total current, but previous studies suggested it is small in our intensity range.[11,20]

For photoelectron emission by s-polarized light from NC-LIPSSs and by both p- and s-polarized lights from a smooth surface, the data are not clear enough for us to extract a slope dependency for intensities below 15 GW/cm^2. For laser intensity higher than 15 GW/cm^2, the slopes of the photoemission currents for the three cases start to show a clear fourth-order dependence and eventually reach 4.5 for p-polarized light from the smooth surface and 4.1 for s-polarized light from both the NC-LIPSS and smooth surfaces, respectively. We notice that the slope for p-polarized light is slightly higher than s-polarized light for the smooth surface at the higher intensity range, indicating that nonequilibrium hot electron heating plays a greater role for the p-polarized case and this is reasonable since light absorption is higher for p polarization. In our experiment, we do not see a noticeable difference for the photoelectron yields from s-polarized light between the NC-LIPSS and smooth surfaces, indicating that nanostructures on NC-LIPSSs do not enhance four-photon photoemission process.

IV. CONCLUSION

We find that SP resonant angle on unique NC-LIPSSs can be significantly different from the calculated angle based on regular periodic grooves. We believe that this SP resonant angle shift is caused by an increase in the real part of the

effective refractive index at the air-metal interface. We also find that the excitation of SPs can significantly enhance photoelectron emission on NC-LIPSSs. Furthermore, nanostructures on NC-LIPSSs relax the phase matching conditions for SP excitation and significantly broaden its angular coupling range, leading to an enhanced photoelectron emission over a broad range of incident angles. Our study shows that NC-LIPSSs are a unique type of structure for enhancing and controlling photoelectron emission.

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