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Formation of high-spatial-frequency periodic surface structures on indium-tin-oxide films using picosecond laser pulses

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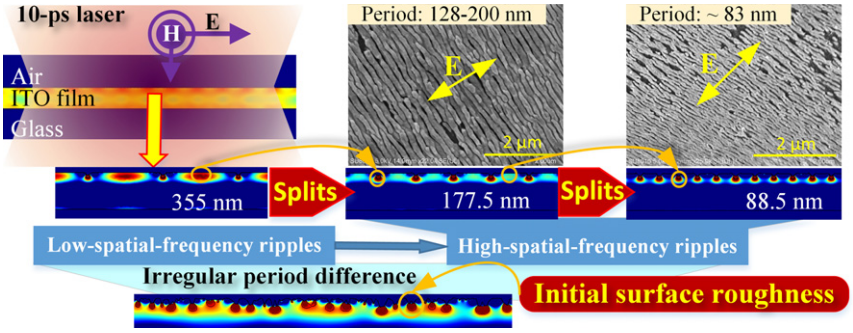
HIGHLIGHTS

- A surface plasmon polariton model with the Drude-Lorentz equation is built.
- The transformation from low-spatial-frequency ripples to high-spatial-frequency ripples is attributed to split.
- The irregular period difference of ripples is attributed to the surface roughness.
- 83-nm-perioded ripples are obtained in accord with the theoretical minimum period of ~88.5 nm.

GRAPHICAL ABSTRACT



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ABSTRACT

A theoretical study, based on the split as well as experiments, was conducted to investigate the formation of high-spatial-frequency laser-induced periodic surface structures (HSFLs) on rough indium-tin-oxide (ITO) films under 10-ps 532-nm-wavelength laser irradiation. At a peak laser fluence of 0.472 J/cm^2, the theoretical periods of HSFLs (130–190 nm) matched the experimental values (128–200 nm). Both the theoretical and experimental results demonstrated that the transformation mechanism of laser-induced periodic surface structures (LIPSSs) from low-spatial-frequency LIPSSs (LSFLs) to HSFLs was attributed to split and the irregular period difference of HSFLs and LSFLs was attributed to the surface roughness. Deeper ablation occurred for LIPSSs with a larger period, and the difference at the ablated depth increased with increasing spot number. Therefore, the LIPSSs with the larger period were clearer demarcated and the initial pits in the convex portion of LIPSSs disappeared due to the laser-induced melting. Consequently, sub-100-nm-perioded HSFLs were invisible in spite of the theoretical minimum period of ~88.5 nm. Then, for pits of different depths, the difference of the ablated depth induced by a subsequent pulse can be narrowed by reducing the laser fluence. On this method, 83-nm-perioded HSFLs were obtained by reducing the peak laser fluence to 0.432 J/cm^2.

1. Introduction

Indium tin oxide (ITO), notable for its high transmittance in the visible spectral region and its low resistivity, has been the material of choice for thin-film solar cells [1–3]. Surface nano-structures, that improve the photo absorption efficiency due to their unique optical and

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physical properties, are essential for the development of the third generation of solar cells [4]. Several studies have investigated both etching manufacturing (plasma dry etching) and additive manufacturing (CVD processes, Au catalytic growth) to obtain the desired nano-structures on the surface of ITO films with periods around 200 nm [4–6]. Increased cost due to the usage of Au and the mold, as well as the complexity of the methods mentioned above, limits their commercial application.

As an emerging technology, laser-induced periodic surface structures (LIPSSs), show regular groove structures with a period on the incident laser wavelength scale. They can be generated in metals, semiconductors, and conducting oxides [7–17], and are attractive for potential applications in surface science and technology with submicron scale. In particular, ultra-short pulsed lasers cause a relatively small thermal-transfer-induced energy redistribution, which is very useful for the creation of periodic surface structures. This occurs because of their ability to create very narrow heat-affected zones due to the extremely short interaction time between the laser light and the material. Upon irradiation of a solid with an ultrafast laser, two types of LIPSS can be distinguished: The first one is low-spatial-frequency LIPSS (LSFL). It has a period close to or slightly smaller than the irradiation wavelength, and an orientation perpendicular to the laser beam polarization. The second type is high-spatial-frequency LIPSS (HSFL). It has a spatial period smaller than half the irradiation wavelength, and an orientation perpendicular but also sometimes parallel to the direction of laser polarization. Recently, some experimental studies have demonstrated the feasibility of HSFL with a period between 100 nm and 200 nm on ITO films using ultrafast laser beams [15–17]. In addition, some experimental studies have demonstrated that HSFL with a period below 100 nm can be formed on the ITO film. Among them, Straub et al. [18] have obtained HSFL with minimum least period down to 50 nm having an orientation perpendicular to laser polarization direction. In this regard, the period of HSFL of ITO with different parameters can vary considerably. It is well known that the obtained minimum period of ITO film shows the limit of laser preparation of LIPSSs. Nevertheless, no systematic research has been conducted on the minimum period of HSFL on the ITO film and its obtainment mechanism so far.

Meanwhile, the formation mechanism of LIPSSs under ultrafast laser pulses has been extensively examined in recent years. In the previous results, laser energy has an influence on the period of LIPSS, where the HSFL can be obtained at the low laser energy [19]. It is generally accepted that these LSFLs were generated by interaction of the incident laser beam with a surface electromagnetic wave (SEW) generated at the rough surface, or excitation of surface plasmon polariton (SPP) [19,20]. While, for HSFL, the formation mechanisms can be explained as self-organization [21,22], second harmonic generation (SHG) [19,23], third harmonic generation (THG) [24], another kind of excitation of SPPs [25], split [26] and cavitation instability [11,27] etc. The self-organization always was used to explain the formation of HSFL with a period parallel to the laser polarization direction or the mixture of nano-dots [28,29]. The THG was induced by surface oxidization, and always targeted to silicon and titanium [24]. For SHG, it is that the LSFL was formed first and second harmonic wave was produced to form the HSFL that has the period half of the period of LSFL [30]. The same phenomenon has been explained as split that was the LSFL induced modification of laser energy distribution. Another kind of excitation of SPPs was that density of free electron increased within pulse duration to produce the HSFL [25]. In addition, the HSFL formed by cavitation instability was always irregular [31]. Among them, only split and SHG were used to explain the transition from LSFL to HSFL with an increase in pulse number, and both of them were characterized of the LSFL formed before HSFL.

For ITO film, The formation mechanism of HSFL with period above 100 nm has been attributed to the SHG [15]. However, the formation mechanism of HSFL with period below 100 nm hasn't been understood well. The split is based on SPP model and always used to explain the formation of HSFL on the surface of metal where the SHG cannot be produced, and seldom used for other materials. For split, if the HSFL with period between 100 nm and 200 nm is obtained, the HSFL with period below 100 nm can be obtained. As a result, it seems that split is suitable for explanation of HSFL with the period below 100 nm. On this basis, the period of the new HSFL can no long reduce by the split of the preformed HSFL, which can be used to compute the minimum period of HSFL on the ITO film.

In addition, unlike material after mechanical polishing, the surface of films obtained by sputtering always has high-frequency waviness, which is dependent of the particle size. It is noted that light self-trapping would occur in the pits so that the locally enhanced laser energy may be large enough to ablate material and modify the period of HSFL [32]. Therefore, the surface roughness also has an influence on the formation of HSFL at a low laser energy. However, the surface-roughness-induced HSFL by SPP has not been taken into consideration.

For SPP model, the electromagnetic field distribution was either based on the Drude equation for free electrons, or the Lorentz equation for bound electrons. ITO is a highly degenerated and wide-band-gap semiconductor with a high electron density. Therefore, its optical properties are not only attributed to free electrons but also to bound electrons. Hence, the Drude-Lorentz model should be verified to be suitable for LIPSS on ITO films [33], which has not been the case in previous studies. Furthermore, the formation of HSFL has not been understood sufficiently, even though their period is thought to be related to the initial surface roughness as well as laser parameters [34].

In this paper, we conduct a theoretical study based on split with the Drude-Lorentz model and an experiment to investigate the formation of HSFL with periods below 200 nm (and even below 100 nm) on the rough ITO film irradiated by 10-ps, 532-nm, laser pulses. The Drude-Lorentz equation was locally modified at the wavelength of 532 nm, and the surface roughness was considered using the Monte Carlo method. In addition, the critical absorbed laser energy density, which represents the critical value above which ITO material can be ablated, was determined. The changing rule of absorbed laser energy density distribution with increasing pulse number was calculated to study the formation mechanism and control methods of the periods of LIPSSs on the ITO film. In addition, the minimum period of HSFL was analyzed by split. Finally, the corresponding HSFL with minimum period was obtained experimentally.

2. Experimental conditions and parameters

A Nd:VAN picosecond laser system (High-Q, IC-1500 ps), which is based on pulse regenerative amplification, was used. The laser system delivers 10-ps-width pulses with a maximum power of 2 W. It works for wavelengths of 1064 nm, 532 nm, and 355 nm. The energy density distribution across the laser beam is Gaussian, with beam quality factor of $(M2) \sim 1.3$. The experimental setup is depicted in Fig. 1. The laser pulse energy is adjusted by using a combination of a half-wave plate and a linear polarizer. A diaphragm is used further to shape the laser beam, and a pyroelectric detector is used to monitor the laser power in real time and in conjunction with a beam splitter in the primary light path. The number of pulses is programmable with an electromechanical shutter. The laser beam is focused and normally incident onto the ITO surface of the sample with the help of a plano-convex lens ($f' = 200$ mm), of which the spot size is 36 μm. A motorized xyz stage (OWIS, PS-30), which is controlled by a computer, is used for precise positioning of the samples. All laser ablation experiments were performed in air and recorded with a CCD camera equipped with a dichroic mirror.

For the present experiment, the pulses with the wavelength of 532 nm and a repetition rate of 1 kHz were irradiated on the sample. The sample was a glass substrate, coated with 180 nm thick ITO films. In addition, the applied laser power densities here were 590, 472 and 432 W/cm^2 to assist the theoretical study and verify the theoretical results. The morphology of the samples was observed with a SEM (HITACHI, SU-8010).