Micro/nano structures fabricated by femtosecond laser on aluminum doped zinc oxide surface

Yanhui Lu¹, Qingsong Wang¹, Changji Pan¹

¹Laser Micro/Nano Fabrication Laboratory, School of Mechanical Engineering, Beijing Institute of Technology, 100081, PR China
Email: luyanhui@bit.edu.cn

Abstract: Nanodot and ripples were fabricated on the aluminum doped zinc oxide (AZO) surface by femtosecond laser irradiation. As increase of laser fluence, the surface of nanodot is smooth and the surface contains numbers nano-cracks due to a strong thermal cycling effect occurrence. The ripples with period approximately 340nm and 660nm were obtained by changing laser fluence and scanning speed. At higher laser fluence, there is a phenomenon that evaporation and redeposition. All of ripples can be explained by surface plasmon polaritons (SPP). In addition, the finite-difference time-domain (FDTD) method is used to simulate and analyze the performance of ripples. The electric field intensity of patterned film is stronger than unpatterned film. Thus, the ripples can be used for improving the photoelectric conversion efficiency of solar energy.

1. Introduction
Over the last decade, the transparent conductive oxide (TCO) material has usually been applied in optoelectronic devices, such as solar cells [1], displays [2], and transparent thin film transistors [3] as a result of having excellent optical and electronic properties. Compared to the other widely used TCOs, for example, indium tin oxide (ITO), aluminum doped zinc oxide (AZO) offers the advantage of being a lower cost, lesser toxicity material abundant [1]. In addition, duo to the multifunctional properties of ZnO such as UV and visible emission, piezoelectric and ferroelectric behavior, and dilute ferromagnetism with appropriate doping, the AZO material with all of the properties is special to other TCOs [4]. AZO with conductivity enhancement and improved transparency can act a potential candidate to be a substitute for ITO material [5]. Especially, in solar cells, AZO film can serve dual purpose of solar spectrum converter from UV to visible for improving light conversion efficiency. There are various methods to fabricate AZO films, such as magnetron sputtering [6], pulsed laser deposition [7], chemical vapor deposition [8] and sol-gel [9]. While, the AZO film fabricated by the above methods can’t meet the demand that fabricating nanostructures on the film surface.

Recently, with the introduction of femtosecond laser amplifier, nanostructures on the surface of materials can be fabricated by illuminating with a femtosecond pulse laser [10, 11]. Femtosecond laser with advantages that wide material adaptability, minimized heat-affected zones, reduced recast is appropriate in fabricating TCO materials surface nanostructures. Cheng et al. [12] induced periodic nanostructures in amorphous ITO films by using femtosecond laser. Wang et al. [13] generated periodic nanodot and nanoline structures on ITO films. By femtosecond laser pulse shape, Ramazan Sahin [14] obtain nanogroove on ITO surface. In the field of fluorine-doped tin oxide (FTO), Han et al [15] fabricating large-scale ripples on FTO films by femtosecond laser irradiation. Li et al. [16] study the surface morphology of FTO films irradiated by laser. Moreover, Xu et al. [17] fabricated large-area
two-dimensional periodic nanostructures on ZnO crystal. However, previous studies were mostly focused on ITO or FTO, few studies have focused on the AZO nanostructures induced by femtosecond laser.

In this work, we have fabricated two nanostructures that nanodot and ripples on commercial AZO films by femtosecond laser irradiation. The scanning electron microscope (SEM) images of all structures have been studied. The surface on nanodot is smooth than original surface and it contains nano-crack due to the accumulation of heat. The ripples with periodic ~340nm and ~660nm can induced by change laser fluence and the speed of platform. In addition, the electric field change caused by ripples have been simulated by finite-difference time-domain (FDTD).

2. Material and methods
In this experiment, the femtosecond laser is a commercial regenerative Ti: sapphire femtosecond laser system (Spectra-Physics) which provides a fundamental Gaussian mode with a central wavelength of 800 nm, pulse duration of 50 fs, and repetition rate of 1 kHz. The experimental set up can been seen in figure 1. In the experimental, the attenuation plate is used to control the laser fluence, and the half-wave plate is used to transform the incident light to linearly polarized light. The laser light is focused through a 10× microscope objective (Olympus, NA=0.3) on the materials. The pulse number (N) delivered to the sample is controlled by a fast mechanical shutter synchronized with the laser repetition rate. AZO contained 3% Al (Kejing Hefei) with a thickness of approximately 700nm is deposited on glass substrate (10mm×10mm×2mm) by magnetron sputtering. The AZO is mounted on a computer-controlled, six-axis moving stage (M-840.5DG, PI, Inc.) with a positioning accuracy of 1μm in the x and y directions and 0.5 μm in the z direction. An and a charge couple device (CCD) is used to observe the fabrication process. Along the white light source, the surface image of sample can be seen. All experiments are carried out in air at room temperature. After irradiation, the surface morphology is characterized by a scanning electron microscope (SEM; Hitachi S4800).

3. Results and Discussion

3.1 Nanodot array by femtosecond irradiation
Figure 2 (a) and (b) show the typical SEM image of AZO films with nanodot array induced by linearly polarized femtosecond laser single pluses. The nanodot with period is 5μm can be obtained by controlling the repetition rate is 100 Hz and the speed of platform is 500μm/s. For the case of fluence (F) = 0.81 J/cm², the size of the nanodot is approximately 3 μm. It can be seen in SEM image, the original surface of the AZO is granular and rough, while the surface of nanodot in Fig. 2(a) is smooth due to the modification by femtosecond laser irradiation. And, at fluence of 1.89J/cm², the diameter of nanodot in Fig. 2(b) is approximately 5μm. With the increase of laser fluence, the size of nanodot is more and more greater. While, it is obvious that nano-crack on the surface of nanodot and the nano-crack is grow as the increase of laser fluence. Previous studies have shown that the high
repetition rate femtosecond laser (i.e. >200 kHz) can minimizes the thermal cycling effect between successive laser pulses and therefore suppresses nano-crack formation when processing bulk transparent glasses [18]. While, the current repetition rate of femtosecond laser is 1 kHz, it is necessary to calculate the cool time [19]. The effective cool time can be calculated by [20]

\[ t_c = \frac{d^2}{D} \]  

(1)

Where \( d_c \) is the diameter of the focused laser beam spot, and \( D \) is the thermal diffusivity of AZO material.

When the \( t_c \) is lower than the time interval between neighbor pulses, there will be a strong thermal cycling effect occurs on the AZO film.

3.2 Ripples induced by femtosecond laser

The SEM images presented in Figs. 3(a)–(f) show the process that ripples with period approximately 340 nm have been fabricated. At the fluence of 0.27 J/cm\(^2\), the AZO can be modified by femtosecond laser and as the increase of laser fluence, the ripples begin to be induced (in Fig. 3(b) and 3(c)). While, the energy accumulation is not enough for inducing ripples, thus it can’t form regular ripples. When the laser fluence is 0.43 J/cm\(^2\), the regular ripples can be observed on the surface, as shown in Fig. 3(d). And continue to increase laser fluence, the ablation can been seen on ripples. When the laser fluence at 0.54 J/cm\(^2\), obviously, the AZO film be ablated over and the glass substrate is exposed (the black in Fig. 3(f)). Because the characteristic of gauss beam accords with Gaussian distribution, the field strength in the central region is higher than edge and it can be explain that the center of ripples have been removed at first.

Figure 3. SEM image of ripples. Note that the scanning speed is 100 μm/s in every case and the laser fluence is specified as follows: (a) 0.27 J/cm\(^2\); (b) 0.32 J/cm\(^2\); (c) 0.38 J/cm\(^2\); (d) 0.43 J/cm\(^2\); (e) 0.49 J/cm\(^2\); (f) 0.54 J/cm\(^2\)
However, there are differences between irradiating at higher laser fluence and irradiating at lower laser fluence. According to Nian et al. [21], as higher laser fluence causes ablation of material, laser evaporated material would redeposit back on the surface, so that there is melting on the resultant surface. Obviously, at the high fluence of 0.81J/cm², the surface of the AZO material is melted. All of the speed from 200μm/s to 700μm/s can induce ripples on the surface at the laser fluence of 0.81J/cm². When the scanning speed is slower, excessive laser pulse will destroy the ripples (in Fig. 4(a)). And when the scanning speed is faster than 700μm/s, the energy accumulation is not enough for inducing ripples. So, at the laser fluence of 0.81J/cm², the most suitable scanning speed is 400-600μm/s. We guess that the process of laser incucing ripples can be divided into two processes. Firstly, the AZO surface was evaporated when the first laser pulse irradiation. The pulse interval is 0.001s and the AZO evaporated can’t be deposited on the surface. Even if the material can be cooled in a short time, the follow pulse also evaporating materials. So, the AZO is not solid throughout the processes. Next, the follow pulse interaction with evaporated material and forming ripples on the surface.

Figure 4. SEM image of ripples. Note that the laser fluence is 0.81 J/cm² in every case and the scanning speed is specified as follows: (a) 200μm/s; (b) 300μm/s; (c) 400μm/s; (d) 500μm/s; (e) 600μm/s; (f) 700μm/s

The mechanism of formatting ripples can be explain by surface plasmon polaritons (SPP). The formation of structures induced at lower laser fluence is explained by interference of the incident and light scattered from the surface based on Sipe’s model [22]. The period is given by [23, 24, 25]

\[ \Lambda = \frac{\lambda}{n_e} \]  

Where \( \lambda \) is the wavelength of the incident laser and \( n_e \) is the real parts of the refractive index.

The ripples induced at higher laser fluence were attributed to the plasmonic wave with period [23, 26]

\[ \Lambda' = \frac{\lambda_{sp}}{2} \]  

Where the wavelength of SPP \( \lambda_{sp} \) is dependent on the plasma density (hence permittivity) and is defined by

\[ \lambda_{sp} = \frac{2\pi}{k_{sp}} = \frac{2\pi c}{\omega n_e} = \frac{\lambda}{n_e} \]  

Thus the period can be expressed by

\[ \Lambda' = \frac{\lambda_{sp}}{2} = \frac{\lambda}{2n_e} \]  

The ratio of the theoretical period of the first structure to that of the second structure is 2, in accordance with the experimental results.
3.3 FDTD simulation

The patterned TCOs exhibits various advantage than flat TCOs, Aaswath et al. [27] proved that the grating structures can increase the photocurrent density in solar cells by using a rigorous coupled wave analysis (RCWA) method. In this simulation, the finite-difference time-domain (FDTD) method is used to simulate and analyze the performance of ripples with period 660 nm. The incident light with wavelength range from 400 nm to 800 nm was launched upward through unpatterned and patterned film respectively and the monitor is placed at the center of substrate. Figure 5(a) show the electric field distribution of unpatterned film, it can be seen clearly that the electric field distributed uniform on the surface and the value approximate 0.13. However, for the film with ripples, the electric field is stronger than unpatterned film. The electric field is focused on ripples and it is two times than unpatterned film. The light trapping can be described the phenomenon than electric field enhanced in Fig. 5(b). The ripples increases the path length of light inside the AZO and reduces the reflection on the surface. The nanostructure can be used in solar cell to increase the photoelectric conversion efficiency.

![FDTD simulation of AZO film. (a) Electric field intensity distribution of unpatterned film. (b) Electric field intensity distribution of ripples with period 660nm](image)

4. Conclusion

Nanodot and ripples were fabricated on the AZO surface by femtosecond laser irradiation. By adjusting laser repetition rate is 100 Hz and the scanning speed is 500μm/s, nanodot arrays with period 5 μm are obtained on AZO. As the laser fluence increase, the diameter of nanodot is increasing. And the nano-cracks on the nanodot were contained on the nanodot due to a strong thermal cycling effect. Next, by changing one of laser fluence and scanning speed, ripples with period 340 nm and 660 nm were fabricated. At higher laser fluence, the processes inducing ripples is different form at lower laser fluence. At higher laser fluence, the material is evaporated and then redeposited on the surface. Finally, the FDTD method is used for simulating variation of electric field intensity. The ripples is effective in enhancing electric field owing to the nanostructures can increases the path length of light inside the AZO reduces the reflection on the surface. This nanostructures have considerable potential in increasing the photoelectric conversion efficiency.

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