Effects of polarization direction on removal characteristics of silver nanowire transparent conductive film by ultrashort pulsed laser

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Abstract
Silver nanowire transparent conductive film is expected as a new material of transparent electrode, because of its superior flexibility and electrical conductivity with transparency at visible wavelength. It is essential to form insulation areas on the silver nanowire transparent conductive film in electronic circuit. Laser beam processing has been widely used for this application, since high efficiency and high quality removal is possible without mechanical contact. On the other hand, laser beam is an electromagnetic wave, and it has unique characteristics such as refraction and polarization. These characteristics have a great influence on laser-material interaction, especially in nanosize materials. However, laser processing characteristics and its mechanism have not yet been clarified. Therefore, polarization indicated by electric and magnetic fields was discussed in this study, and effects of polarization direction on removal characteristics of silver nanowire transparent conductive film by ultrashort pulsed laser with linear polarization were experimentally and numerically investigated. Removal phenomena of silver nanowire transparent conductive film by linear polarization was different from that by circular polarization. Silver nanowires arranged in the parallel direction to polarization plane were preferentially removed. In the case of crossed two silver nanowires, electromagnetic field analysis revealed that electric field intensity of silver nanowire arranged in parallel direction to polarization plane is higher than that in perpendicular direction to polarization. Therefore, silver nanowires were selectively removed depending on the polarization plane of laser beam. Electric field intensities of silver nanowire arranged in not only parallel but also perpendicular direction to polarization plane were enhanced at intersection of silver nanowires, and holes as removal marks become remarkably large at intersections of silver nanowires.

Keywords: Silver nanowire, Transparent conductive film, Ultrashort pulsed laser, Polarization, Electric field analysis, Removal

1. Introduction

Recently, transparent conductive film has been widely used as an important material for electrics devices, because it has high transparency at visible wavelength and conductivity similar to general metals. In particular, ITO (Indium Tin Oxide) films have been widely used as a transparent conductive film because of its superior electrical and optical properties. However, ITO has a problem in sustainable use, because ITO contains indium as a rare metal. In addition, ITO is brittle, and its flexibility is low. Both high conductivity and high flexibility are required for transparent conductive film in industrial application such as thin films solar cells, flat panel displays and touch panels. Recently, silver nanowire
transparent conductive film is expected as an alternative material to ITO film (Huang and Huang 2014). Silver nanowire transparent conductive film has superior flexibility according to the use of PET (Polyethylene terephthalate) substrate, and it also has good conductivity and high transparency at visible wavelength. In addition, silver nanowire is mainly manufactured by the polyol process, it is easy to scale up with low cost and good uniformity (Guzman and Balela, 2013).

It is essential to create insulation areas on the silver nanowire transparent conductive film in electronic circuits. Silver nanowire transparent conductive film has conductivity by contacting silver nanowires. Therefore, selective removal of silver nanowires is necessary to create electric circuits for a silver nanowire transparent conductive film (Medvedovski et al, 2009). Laser beam processing has been widely used for the removal of transparent conductive film, since high efficient and high qualitative removal is possible without mechanical contact (Exarhos, 2009). In recent years, it has been reported that nanostructured materials have accompanied unprecedented optical properties. Photon reaction of nano-scale material has become a major research area, and has been making important advances in several industrial applications, such as information technologies, energy, high-density data storage, life sciences, and security (Anatoly and Stefan, 2013). On the other hand, laser beam is an electromagnetic wave, and it has unique characteristics such as refraction and polarization. These characteristics have a great influence on laser matter interaction, especially in nanosize materials. However, laser processing characteristics of nano-scale materials and its mechanism have not yet been clarified. Therefore, the polarization indicated by electric and magnetic fields was discussed in this study, and effects of polarization on removal characteristics of silver nanowire transparent conductive film by using ultrashort pulsed laser with linear polarization were experimentally and numerically investigated.

2. Experimental setup and specimen

2.1 Laser irradiation method

Figure 1 shows schematic diagram of optical setup. Ultrashort pulsed laser was used in this experiment. The center emission wavelength and pulse repetition rate were 790 nm and 1 kHz, respectively. Silver nanowire transparent conductive film fixed on xyz stage was irradiated by ultrashort pulsed laser with a focusing lens of 150 mm in focal length. Overlap rate was controlled by scanning speed at fixed pulse repetition rate of 1 kHz. The edge of processing line by circular laser beam becomes wavy shape, because it is created by the sum of laser shot of circular shape with Gaussian-mode intensity distribution. Therefore, square-shaped laser beam with top-hat mode is useful to create straight processing lines. In this study, laser beam of Gaussian-mode from the oscillator was formed into top-hat beam mode with a square mask of 1.5 mm by 1.5 mm. The distance between the square mask and the focusing lens was approximately 2500 mm, and the distance between the focusing lens and the silver nanowire transparent conductive film was approximately 160 mm to obtain the sharp image of the square mask. In this optical setup, top-hat intensity distribution of approximately 80 µm square spot was obtained at the imaging plane at 10 mm far from the focusing point.

2.2 Silver nanowire transparent conductive film

In this experiment, silver nanowire transparent conductive film was used as a specimen. Figure 2 schematically shows the structure of silver nanowire transparent conductive film. Silver nanowire transparent conductive film is
covered by an acryl overcoat layer containing the silver nanowires on PET (Polyethylene terephthalate) of substrate. Figure 3 shows top and cross sectional views of silver nanowire transparent conductive film. Silver nanowires of approximately 80 nm diameter and 15 µm length are distributed in the whole area of the overcoat layer. The thickness of the overcoat layer containing silver nanowires is approximately 2 µm, and the total thickness of the specimen including PET substrate is 120 µm. In this experiment, silver nanowires was irradiated with laser beam from the overcoat layer side at the imaging plane.

3. Effect of linear polarization plane on processing characteristics of silver nanowire

Both circular and linear polarized laser beams were used to remove silver nanowires, and the effect of linear polarization plane on processing characteristics is evaluated. The number of laser shot per point is one (N = 1), and an individual laser shot remains under no-overlapping condition. Fluence is pulse energy per unit area, and it is calculated by Eq. (1).

\[ F = \frac{E}{S} \]  

where, \( F \) is fluence, \( E \) is pulse energy, and \( S \) is area irradiated with laser.

3.1 Comparison of processing results by laser beam with circular and linear polarization

Figure 4 shows Scanning Electron Microscope (SEM) photographs of silver nanowire film by using the laser beams with circular and linear polarizations. Pulse duration of 10 ps and fluence of 1.0 J/cm² were used for both cases. The removal phenomena of silver nanowire transparent conductive film by laser beam with linear polarization was different from that by circular polarization, as shown in SEM photographs. Silver nanowires arranged in particular direction were
preferentially removed by the linear polarized laser beam, while the circular polarized laser beam removed silver nanowires regardless of the direction of silver nanowires. Next, effects of linear polarization plane on removal characteristics were experimentally investigated.

**3.2 Processing characteristic by linear polarization with parallel and perpendicular direction to scanning line**

Figure 5 shows SEM photographs of silver nanowire film with the linear polarized laser beam in parallel and perpendicular directions to scanning line. Pulse duration and fluence were 200 fs and 0.8 J/cm², respectively. Processing results revealed that silver nanowires arranged in parallel direction to polarization plane were preferentially removed. This phenomenon indicates that the laser energy absorption to silver nanowires arranged in parallel direction to polarization plane would be larger than those arranged in perpendicular direction to polarization plane. Under this condition, silver nanowires arranged in parallel direction to polarization plane were preferentially removed, but these removal areas were not continuous lines, which were recognized as dotted removal areas. These phenomena suggest that there are different areas, where is easy or difficult to be excited, although silver nanowires were arranged in the same direction to polarization plane. In addition, preferential removal can be observed at the intersections of the silver nanowires regardless of the direction of silver nanowires arrangement, which suggests that silver nanowires are easy to be excited at the intersections.

Figure 6 shows surface appearance of the specimen for various fluence by linear polarized laser beam in parallel direction to scanning line. Pulse duration were 200 fs. Silver nanowires arranged in parallel direction to polarization plane were recognized as dotted removal areas in the same phenomena of previous processing results as shown in Fig. 5. Removal areas were connected, and became continuous lines with increasing the fluence. In addition, at fluence of 1.2
J/cm², silver nanowires arranged in neighborhood of perpendicular direction to the polarization plane were also removed. These phenomena indicate that sufficient energy to remove silver nanowires was absorbed by increasing the fluence, even if silver nanowires were not arranged in the correctly parallel direction to polarization plane, where laser beam energy was not absorbed at lower fluence. Next, these processing phenomena and characteristics were numerically investigated by using electromagnetic field analysis.

4. Electromagnetic field analysis of silver nanowires

Free electrons on the material surface are shaken by irradiation of laser beam, and the photon energy is converted into the vibration of lattice, which results in the ablation of material. Silver nanowires are removed by ablation process, and it is important to understand the intensity distribution of laser beam on silver nanowires. Since the laser beam is an electromagnetic wave, the electromagnetic intensity distribution on the surface of silver nanowires is useful to discuss the intensity distribution of laser beam.

On the other hand, electromagnetic wave is the wave which alternatingly propagates in electric and magnetic fields. When electric and magnetic fields strike matter, the effect of electron movement generates much stronger electric field than magnetic one (Guenther, 2015). Since laser beam is one of the electromagnetic field, effect of electron movement would contribute the heating of material. Therefore, the intensity distribution of laser beam on the surface of silver nanowires was calculated using finite element method. Here, electric field was investigated, when the silver nanowire transparent conductive film was irradiated by laser beam.

4.1 Wave equation in time-harmonic electromagnetic field analysis

The intensity distribution of electric field was calculated by using Eq. (2). Time-harmonic electric wave equation is obtained from Maxwell’s equation (Saiki and Toda, 2009),

$$\nabla \times (\mu_r^{-1} \nabla \times E) - k_0^2 \varepsilon_c E = 0$$  \hspace{1cm} (2)

where $\mu_r$ is the relative permeability, $E$ is electric field intensity, $k_0$ is the wave number of the electromagnetic field in vacuum, and $\varepsilon_c$ is the complex permittivity. This electromagnetic field analysis was assumed as the time-harmonic, and electromagnetic field was dealt as the harmonic vibration of angular frequency $\omega$. Wave number $k_0$ is obtained by Eq. (3).

$$k_0 = \frac{\omega}{c_0}$$  \hspace{1cm} (3)
where $c_0$ is the light speed in vacuum. The model of analysis was developed for a silver nanowire transparent conductive film contained in an acrylic layer. It is necessary to determine numerical value of the relative permeability $\mu_r$ and complex permittivity $\varepsilon_c$ to calculate the wave equation of two materials. The relative permeability $\mu_r$ of the acrylic and the silver were set to $\mu_r = 1$ and $\mu_r = 0.99998$, respectively (Harold and Darren, 2013). Complex permittivity $\varepsilon_c$ is adapted by Eq. (4) considered the complex permittivity in material for the acrylic, and Eq. (5) considered the complex permittivity of conductor for the silver.

$$
\varepsilon_c = (n - i\gamma)^2
$$  \hspace{1cm} (4)

$$
\varepsilon_c = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2}
$$  \hspace{1cm} (5)

where $n$ is the refractive index, $i$ is the imaginary unit, and, $\gamma$ is the damping coefficient. Since the light absolution rate of overcoat layer in silver nanowire transparent conductive film is very small, the damping coefficient was determined as $\gamma = 0$ to simplify the analysis, and the refractive index was set to $n = 1.5$ with the consideration of wavelength dependence (Amaresh and Edmond, 2002). Eq. (5) used Drude model, and the permittivity of high-frequency was set to $\varepsilon_{\infty} = 1$, the plasma frequency was $\omega_p = 1.4 \times 10^{16}$ s$^{-1}$ in silver (Christopher and Richard, 2010), (Wenshan and Vladimir, 2010). Angular frequency $\omega$ of electromagnetic field was $\omega = 1.27 \times 10^{6}$ s$^{-1}$, because ultrashort pulsed laser used in the experiments had the wavelength of 790 nm. When electric field intensity was assumed as $E = 1$ V/m, electric field intensity was calculated by using these equations to discuss relative difference.

4.2 Model and conditions of electromagnetic field analysis

COMSOL Multiphysics, which is a commercial software for finite element method, was used for electromagnetic field analysis. This analysis calculated the electric intensity distribution on the surface of silver nanowires, when two crossed silver nanowires in silver nanowire transparent conductive film were irradiated by laser beam. Figure 7 shows the model of the analysis. Columnar silver nanowires of 80 nm diameter and 1 µm length were intersecting in this model, and there were 10 nm distance between two silver nanowires to obtain converged solution. The origin of xyz-axes was the center of entire model. Here, x-axis was set as the direction of silver nanowire located on the upper part, and y-axis was the direction of silver nanowire located on the lower part. The polarization plane was defined in both perpendicular and parallel directions to x-axis in this analysis.

Figure 8 shows element sizes in this analysis model. The maximum length of one side was less than one-eighth of 790 nm wavelength. In x-axis, silver nanowires of 1 µm length was divided into 5 parts, and the intersecting area was divided into 5 parts as well. In the radial direction of silver nanowire, the circumference was divided into 34 parts filled with triangle elements.

Fig. 7 Analytical model of crossed silver nanowires in electromagnetic field analysis by perpendicular polarization to x-axis.
4.3 Analysis results and discussion

Figure 9 shows the analysis results of electric field on the surface of crossed silver nanowires, and electric field distributions were shown relatively. The left column shows the model, upper row shows the analysis results observed from the plus direction of y-axis, the middle row shows that from the plus direction of x-axis, and the bottom row shows that from the first quadrant. The middle column shows the analysis results in the case of linear polarization parallel to x-axis, which means the polarization plane is parallel to the upper silver nanowire. The right column shows that of perpendicular direction to x-axis, which indicates the polarization direction is parallel to the lower silver nanowire.

Judging from the analysis results of Fig. 9, the intensity of electric field on the silver nanowire located in parallel direction to the polarization plane was enhanced in both cases of the polarization plane. Furthermore, high and low electric intensity areas were observed in the axis direction of silver nanowires located in parallel to polarization plane. As shown in Figs. 4 and 5 as processing results, the energy absorption of laser beam became higher on silver nanowires located in parallel direction to polarization plane compared with that located in perpendicular direction to polarization plane. In addition, it was suggested that there was spatial difference of the energy absorption in axis direction of silver nanowires, and analysis results agree well with the experimental results, in which removal marks were observed as dotted lines. On the other hand, the electric intensity on the silver nanowire located in perpendicular direction to the polarization plane was relativity higher at the intersections of silver nanowires compared with that in other areas. This tendency corresponds with the processing results that preferential removal were relatively observed at the intersections of silver nanowires regardless of direction of silver nanowires. Since the electric intensity at the intersection of both upper and lower silver nanowires became stronger than the surrounding area, it is considered that preferential material removal was occurred at the intersection of silver nanowires.

![Electric field on surface of crossed silver nanowires.](image)
5. Conclusions

In this study, the effects of polarization plane on removal characteristics of silver nanowire transparent conductive film by ultrashort pulsed laser with linear polarization were experimentally and numerically investigated. Main conclusions obtained in this study are as follows:

1. Removal phenomena of silver nanowires by linear polarization was different from that by circular polarization. Silver nanowires arranged in particular direction were preferentially removed by linear polarized laser beam, while circular polarized laser beam removed silver nanowires regardless of directional arrangement of silver nanowires.

2. In the crossed silver nanowires, the electric intensity of silver nanowire in parallel direction to linear polarization plane was periodically enhanced, and the removal areas were periodically created.

3. Electric field intensities of silver nanowire arranged not only in parallel but also in perpendicular direction to polarization plane became higher at intersection of silver nanowires, and holes as removal marks became remarkably large at intersections of silver nanowires.

References