A new method to characterize the metallic-oxide films for grayscale lithography*

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In order to characterize the metallic-oxide grayscale films fabricated by laser direct writing (LDW) in indium film, a new method with micro-Raman spectroscopy and atomic force microscope (AFM) is proposed. Raman spectra exhibit the characteristic band of In_2O_3 centered at 490 cm^{-1}, in which the intensities increase with the decreasing optical density of the In-In_2O_3 grayscale films. The mapping information of Raman spectra shows that the signal intensities of the film in the same grayscale area are uniform. Combining with the information of In-In_2O_3 grayscale film from AFM, the quantitative relationship between the concentration of In_2O_3 and the Raman signal intensity is shown. Compared with the conventional methods, the resolution of micro-Raman scattering method is appropriate, and the scanning speed is proper to analyze the structure of metallic-oxide grayscale films.

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Laser direct writing (LDW) is a precise and convenient micro/nano fabrication technology. The metallic-oxide grayscale films fabricated by LDW play an important role in grayscale lithography for creating three-dimensional (3D) microstructures, such as micro-electro-mechanical systems (MEMS) and micro-optics[1-4]. In-In_2O_3 is one of the typical materials of grayscale film, which has significant applications in the field of transparent conductive films, such as gas sensors, flat panel displays, transparent electrode materials, solar cells and electroluminescent diodes[5-9].

The structural stability of polycrystalline films has strong influence on the stability of the thin film devices. Therefore, it is necessary to find a precise and convenient method to characterize the films fabricated by LDW. There are many classical methods to analyze the film sample, such as transmission electron microscope (TEM), selected area electron diffraction (SAED), transmission spectrum, scanning electronic microscope (SEM) and atomic force microscope (AFM)[10-14]. These conventional methods are able to illustrate the properties of grayscale films, but they also have different instinct drawbacks in characterizing grayscale films. TEM and SAED can analyze the content of the film sample, and the resolution can reach less than 100 nm. But both of them are not suitable to scan a sample in a large scale due to the time-consuming acquisition. SEM and AFM can show the surface topography of film samples, but they can not present the content of samples directly. It is convenient to obtain the optical density of grayscale film by transmission spectrum, but this method is not suitable to analyze the sample fabricated by LDW, because the resolution cannot reach sub-micrometer scale.

In this paper, we present the micro-Raman spectra to characterize the metallic-oxide grayscale films fabricated by LDW. In general experimental environment, micro-Raman spectrometer can provide the information about the transformation of crystalline, the change of the crystal grain size and the inner structure of samples. It is not necessary to pretreat or damage the samples, put them in vacuum, etc. Moreover, the resolution of this method can reach sub-micrometer scale, and the scan scale is relatively large. Micro-Raman spectrometer is used to analyze the In-In_2O_3 grayscale film. Raman spectra exhibit that one characteristic band of In_2O_3 centers

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at 490 cm^{-1}. The Raman signal intensity increases with the decreasing optical density of the In-In_2O_3 grayscale film, and the signal intensities of the film are uniform in the same grayscale area. Combining with the information of In-In_2O_3 grayscale film from AFM, the quantitative relationship between the concentration of In_2O_3 and the Raman signal intensity is presented.

Indium films with a thickness of 25 nm and a roughness (Rq) of 2 nm were sputtered on glass substrates by radio-frequency magnetron sputtering (ULVAC ACS400-C4). A Nd: YAG 532 nm laser was used as the beam source of a laser direct writer, and the sample was placed on the focal plane of the objective lens with numerical aperture (NA) of 0.95 (Nikon). The laser power ranges from 2.4 mW to 8 mW, and the pulse width is hundreds of nanoseconds. A bitmap file, which is transformed automatically from an original picture, defines the laser power of each pixel, the writing path and the pixel stepping (50–200 nm, typically 150 nm). We used LDW to fabricate indium films with five different laser power levels of 8.0 mW, 6.6 mW, 5.2 mW, 3.8 mW and 2.4 mW. Therefore, the indium film was oxidized in different levels, and the concentration of In_2O_3 is different in different areas. In Fig.1, we show the optical image of In-In_2O_3 film with five grayscales (a-e) for different laser power levels.

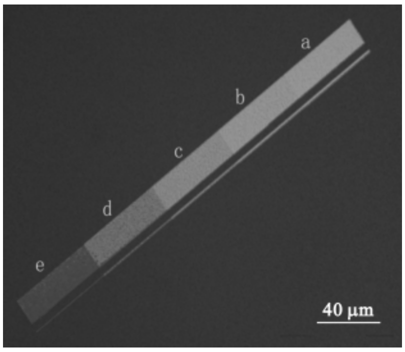

Fig.1 Optical image of In-In_2O_3 film with five grayscales for different laser power levels of (a) 8 mW, (b) 6.6 mW, (c) 5.2 mW, (d) 3.8 mW and (e) 2.4 mW

The gray levels are realized by adjusting the writing power, because laser irradiation can heat the local domain of indium film and turn indium into transparent In_2O_3, and the higher power yields a higher transmittance. In the interaction of a laser beam with a metallic film, the absorption part of the laser's energy converts to heat, making temperature rising and metal oxidatized. The brighter areas are exposed by higher laser power. The gray levels and fine structures of grayscale patterns in indium films imply that the grayscale films can be used for high-resolution grayscale lithography.

Micro-Raman spectra as shown in Fig.2 were acquired by a micro-Raman spectrometer (Renishaw inVia plus) equipped with an argon ion laser (514 nm) and a triple monochromator (1800l mm^{-1}). A two-dimensional (2D) charge-coupled device (CCD) detector at the exit port of the spectrometer collected both spatial and spectral information originating from the illuminated sample. The actually investigated spectral range is between 200 cm^{-1} and 1400 cm^{-1}. To block In_2O_3 material, which is the body centered cubic (BCC) structure, the Raman signals are at about 130 cm^{-1}, 300 cm^{-1}, 360 cm^{-1}, 490 cm^{-1} and 625 cm^{-1}. The Raman signals of five different grayscales present that the relative intensity is related to the grayscale of the In_2O_3. Raman shifts for the sample of In_2O_3 films are observed at 200 cm^{-1}, 355 cm^{-1}, 490 cm^{-1} and 620 cm^{-1}. The last three peak positions are in good agreement with the reported values, and the FWHM is expanded to about 65 cm^{-1} as shown in Fig.2. The polycrystalline effect leads to the band expansion. As has been clarified, the In_2O_3 exists in polycrystalline state in the film, so every crystal grain can be a micro-Raman scattering source. The Raman signal from each source is a little different from that in the band center. As a superposition result, the Raman peak is expanded. Our micro-Raman characterization of samples is effective to analyze the content of In-In_2O_3 grayscale film.

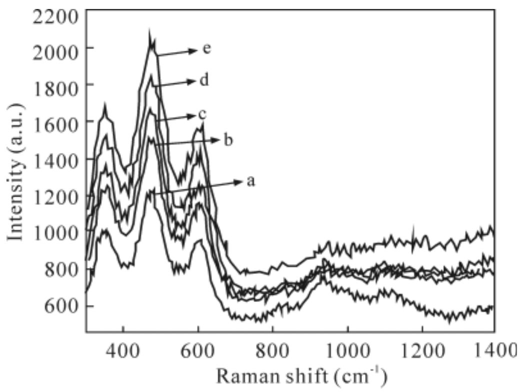

Fig.2 Micro-Raman spectra of In-In_2O_3 film with five different grayscales decreasing from area a to e

Fig.3 is the Raman line-scanning result of the film (at 490 cm^{-1}), which shows that the signal intensities of the film are almost uniform in the same grayscale area.

The Raman mapping result of In-In_2O_3 grayscale film is shown in Fig.4. It presents that the Raman signal intensities are uniform in the area with the same gray level. The result also illustrates that the signal intensities of different areas with the five different gray levels increase with the concentration of In_2O_3.

As has been clarified, the indium film is oxidized as indicated from the Moiré fringes[10]. Therefore, the relative thickness of the film (h) should be larger where the content of In_2O_3 is higher. As expected, AFM topographic images as

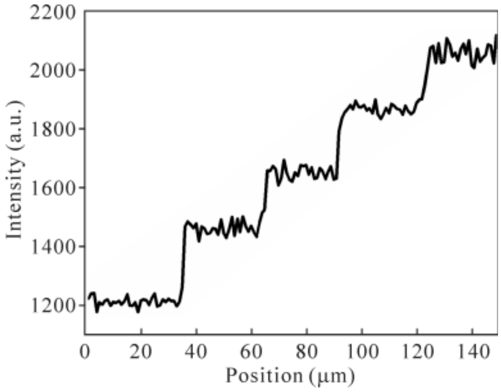

Fig.3 Raman line-scanning result of In-In_2O_3 film at 490 cm^{-1} in five-grayscale area

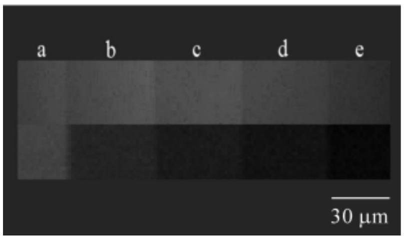

Fig.4 Mapping information of Raman spectra of In-In_2O_3 grayscle film with five different gray levels (a-e)

shown in Fig.5 agree well with optical images, which means that the laser exposed area has not only exact optical image replication in the film plane but also controllable height in the *z* direction.

From the AFM images, we get the relative thicknesses (Δh) of films with different grayscales. Moreover, we know the densities and molecular weights of In and In_2O_3 are ρ_{In}=7.31 g/cm^3, $\rho_{In_2O_3}$=7.18 g/cm^3 and M_{In}=114.8, $M_{In_2O_3}$=227.6, respectively. So we can obtain the quantitative relationship between the concentration of In_2O_3 (x) and the thickness of film as

$$x = 4.33\Delta h/h_0 , \quad (1)$$

where h_0 is the thickness of the substrate, and h_0 is 25 nm in our experiment. Tab.1 shows the results of the concentrations of In_2O_3 (x) and the relative thicknesses (Δh) of films with different grayscales.

Tab.1 Relationship between the concentration of In_2O_3 (x) and the relative thickness (Δh) of film for different grayscales

	a	b	c	d	e
Δh (nm)	1.776	2.682	3.843	4.703	5.695
x	30.76%	46.45%	66.56%	81.46%	98.64%

Furthermore, combining with the information of In-In_2O_3 grayscale film from AFM, the quantitative relationship between the concentration of In_2O_3 and the Raman signal intensity is obtained shown in Fig.6. The Raman signal intensity linearly increases with the increasing concentration of In_2O_3.

So we can use Raman signal intensity to calibrate the concentration of In_2O_3, which is a novel, convenient and efficient method to analyze the structure of metal oxide grayscale film.

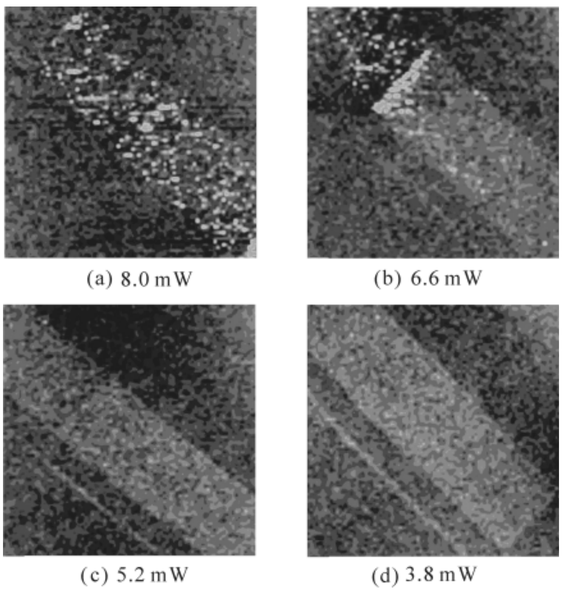

Fig.5 Surface topographies of In-In_2O_3 gray film from AFM for different laser power levels

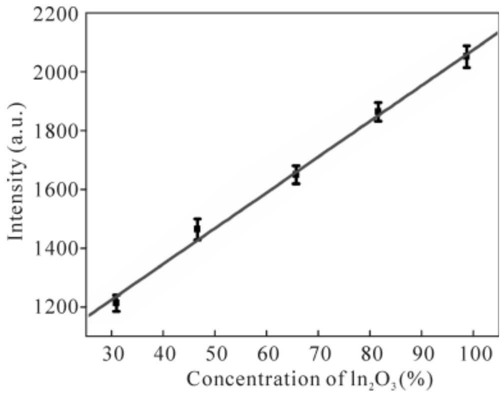

Fig.6 Quantitative relationship between the Raman signal intensity and the concentration of In_2O_3

In conclusion, the grayscale film is fabricated by using LDW technique. The results of TEM and SAED show that there are only two components in the film: In and In_2O_3. The content of In_2O_3 can be controlled by modulating the power of laser. The relative thickness of the film should be larger where the content of In_2O_3 is higher. The micro-Raman spectra show that under the same fabrication condition, the Raman peak at 490 cm^{-1} has the same intensity, which is almost linearly proportional to the concentration of In_2O_3. So we can propose a novel, convenient and precise method to characterize the structure and concentration of the metallic-oxide grayscale films by using micro-Raman spectra combined with AFM, which overcomes the disadvantages of conventional methods.

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