Characteristics of Indium Tin Oxide Films Deposited by DC and RF Magnetron Sputtering

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Conductive and transparent indium tin oxide (ITO) films with a thickness of 100nm were deposited onto glasses and Si (100) wafers by direct current (DC) and radio frequency (RF) magnetron sputtering. The formation and the annealing effect of films were studied by the measurements of resistivity, optical-transmission, X-ray diffraction and scanning tunneling microscopy (STM). Experimental studies indicated those films deposited by DC sputtering in a 1% O_2 in an O_2/Ar gas mixture, without annealing, have the lowest resistivity and the highest transmission. In addition, the films deposited by RF sputtering in a 3% O_2 in an O_2/Ar gas mixture, with annealing in air at 300℃ for 2h, have better resistivity and transmission.

KEYWORDS: indium tin oxide; film; formation; magnetron sputtering

1. Introduction

Because of their high conductivity and transmissivity, indium tin oxide (ITO) films have motivated great interests in experimental studies and technological applications. The exceptional properties of ITO films can be exploited in numerous applications in optical electronic devices, for example, solar cells,[1)] photodiodes,[2-5)] image sensors,[6)] liquid crystal displays,[7)] and charge coupled devices.[8)] In addition, an interesting application of ITO is coating an optical fiber tip for photon- scanning tunneling microscopy (STM) imaging. As the conductive optical fiver tip can inject carriers and collect photons simultaneously, it has been used to study photon emission from adsorbed porphyrin molecules on a metal surface induced by tunneling electron.[9)] Up to date, ITO films have been prepared by various deposition techniques such as chemical vapor deposition,[10,11)] electron beam evaporation,[12)] reactive thermal evaporation,[13)] spray pyrolysis,[14)] direct current (DC) and radio frequency (RF) magnetron sputtering.[15-21)] Among the various deposition techniques, films with the lowest resistivity and the highest transmission have been prepared by magnetron sputtering.[15-17,20)]

Previously, we presented a report on the deposition of ITO films on glasses and Si (100) substrates using DC magnetron sputtering in argon (Ar) atomosphere.[22)] In the report, we systematically studied the influence of growth temperature and a subsequent annealing procedure on the electrical, optical and X-ray diffraction properties. Based on the electrical and optical properties, a realistic substrate

temperature 325℃ for the deposition of ITO films was experimentally found. For improvements in conductive and transparent properties, the deposited ITO films should be annealed in air at 300℃ for 2h. Here we report on the DC and RF magnetron sputtering deposition of ITO on glasses and Si(100) surfaces at

325℃, in argon (Ar) and oxygen (O_2) mixed atmosphere with various O_2 fractions from 0% to 5%. X-ray diffraction, resistivity, transmission measurements and STM observations were carried out to investigate the DC and RF sputtered films. Also the effects of annealing (in air at 300℃ for 2h) on the electrical and optical properties of ITO films are presented.

2. Experimental Procedure

Glasses (80 μm in thickness) and Si(100) wafers (380μm in thickness) were used as substrates. The films deposited on glasses were used in the study of conductive and transparent properties, while the films deposited on Si(100) were used in the study of thickness measurements and STM observations. The deposition of ITO films was performed with the coaxial magnetron sputtering, at a substrate temperature of 325℃, in Ar and O_2 mixed atmosphere using a commercial sputter deposition system **(Eiko Ltd., Japan).** In the mixed atmosphere, the O_2 gas fraction was from 0% to 5%. A disk-shaped hot pressed ITO target (80φ×3T) composed of 95 wt% In_2O_3 and 5 wt% SnO_2 was used. The glass and Si substrates were pre-cleaned with ethanol and acetone, respectively. Before deposition, the substrates were pre-heated from room temperature up to 325℃ and kept for 2h. The substrate temperature was kept constant during the deposition. The distance between the substrates and target is 100mm. Flows of Ar and O_2 gas were controlled by mass flow controllers. The deposition conditions included RF/DC magnetron power of 100W, Ar and O_2 gas mixture at a total pressure of ～1.7×10^{-3}Torr. The deposition rate was ～ 25nm/min.

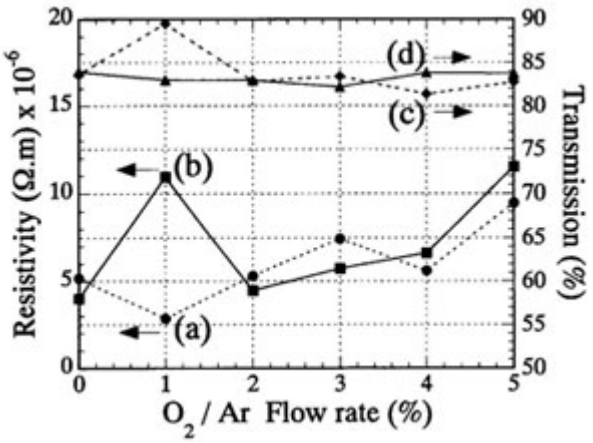

Fig.1. Resistivities and transmission of 100nm thick ITO films on glasses varsus O_2/Ar flow rate (0-5%) before and after annealing in air at 300℃ for 2h. The films were deposited by DC 100W, at substrate temperature 325℃ and under Ar and O_2 mixed pressure of ~1.7×10^{-3}Torr. (a) and (c) are before annealing, (b) and (d) are after annealing.

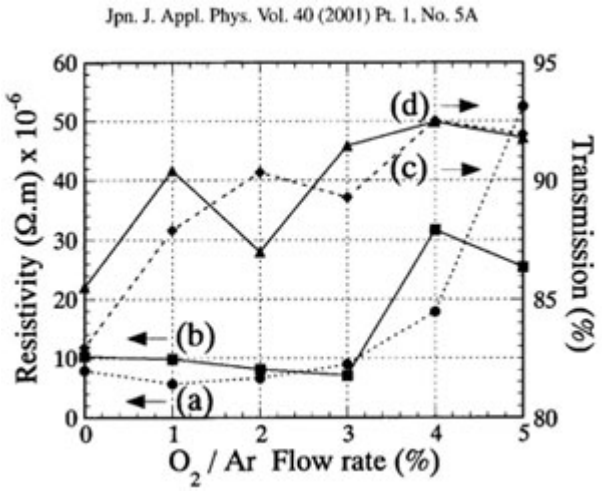

Fig.2. Resistivities and transmission of 100nm thick ITO films on glasses versus O_2/Ar flow rate (0-5%) before and after annealing in air at 300℃ for 2h. The films were deposited by RF 100W, at substrate temperature 325℃ and under Ar and O_2 mixed pressure of ~1.7×10^{-3}Torr. (a) and (c) are before annealing, (b) and (d) are after annealing.

After sputter deposition, the films were annealed in air at 300℃ for 2h. Film thickness was measured with a surface texture measurement instrument. The film resistance was measured by the four-point probe method with a DC voltage current source (R6145). The film transmission was measured with a universal optical power meter (MELLES GRIOT) using a laser wavelength of 650nm.X-ray diffraction data were taken with a Rint 2500 X-ray diffractometer. STM images were obtained with a JSTM-4200s in air.

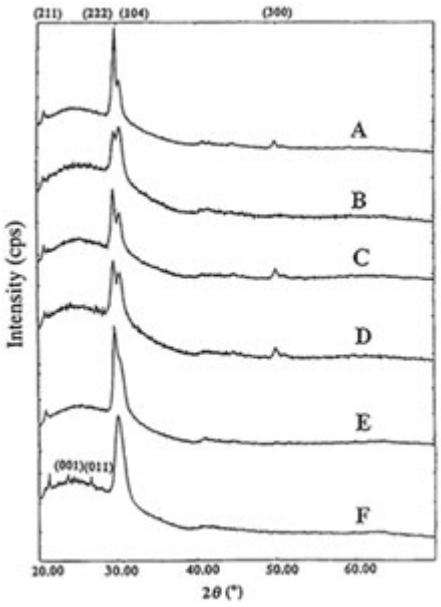

Fig.3. X-ray diffraction pattern of 100nm thick ITO films glasses after deposition and annealing in air at 300℃ for 2h, the films were deposited by DC 100W, at substrate temperature 325 ° , under Ar and O_2 mixed pressure

of ~1.7×10^{-3}Torr in which O_2/Ar flow rate was O%A, 1%B, 2%C, 3%D, 4%E and 5%F.

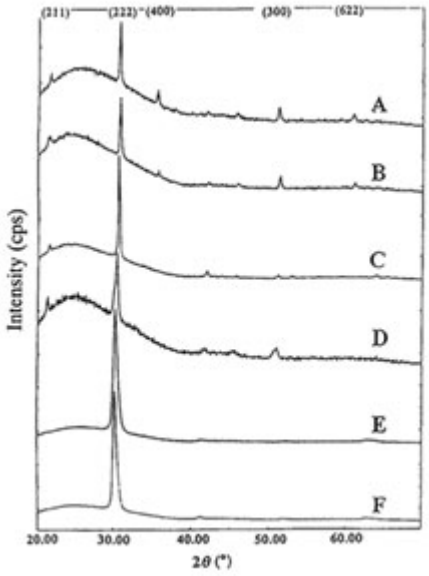

Fig.4. X-ray diffraction pattern of 100nm thick ITO films on glasses after deposition and annealing in air at 300℃ for 2h. the films were deposited by RF 100W, at substrate temperature 325 ° , under Ar and O_2mixed pressure of ~1.7×10^{-3}Torr in which O_2/Ar flow rate was 0%A, 1%B, 2%C,3%D, 4%E and 5%F.

3. Results

3.1 Electrical and optical properties

Figure 1 shows the resistivities and the transmission of ITO films grown by DC magnetron sputtering versus the O_2/Ar flow rate (%) before and after annealing in air at 300℃ for 2h. The resistivity of the film produced without O_2 is used as a reference. In general, before annealing, the resistivity increases with increasing O_2/Ar flow rate. After annealing the resistivity exhibits similar tendency. However, at an O_2/Ar flow rate of 1%, the film without annealing has the lowest resistivity. After annealing, the resistivity increases too much as presented in Fig.1, curves (a) and (b). For films deposited in atomosphere with and without oxygen, there are not so much differences in transmission before and after annealing. Only at an O_2/Ar flow rate of 1%, before annealing, the film shows the highest transmission. After annealing, the transmission decreases obviously as exhibited by comparing curves (c) and (d) in Fig.1. Based on the resistivity and transmission, the film produced by DC 100W under mixed atmosphere pressure of ~ 1.7×10^{-3}Torr with O_2/Ar flow rate of 1% without annealing possesses generally the best conductive and transparent properties. Fig.2 similarly describes electrical and optical properties of ITO films produced by RF magnetron sputtering. By using the same analysis and comparison, it is found that the film deposited with O_2/Ar flow rate of 3% and annealed in air at 300℃ for 2h exhibits the better conductive and transparent

properties.

It is clearly seen in Fig.1 that we found the singularity in resistivity and transmission of the ITO films grown by DC sputtering in Ar and O_2 mixed atmosphere with 1% O_2. To our knowledge, the singular phenomenon was not reported before. The exact reason is still not clear to us. From Figs.1 and 2, the effect of the presence of oxygen gas in the sputtering atmosphere on the film properties, especially on the film resistivity, is remarkable. The influence of oxygen flow rate on resisitivity can be explained in terms of two competing effects.[15, 20)] Increase in oxygen flow rate enhances the growth of crystalline phases of ITO films which leads to higher mobility of carriers.[23)] On the other hand increased oxygen flow rate decreases the carrier density.[24)] The good electrical conductivity of ITO films depends on doping with Sn^{4+} at In^{3+} sites in the In_2O_3 lattice.[25)] O-hole defects generate *two* electrons as carrier and *one* electron is generated when In^{3+} is substituted by Sn^{4+}.[26)]

3.2 X-ray diffraction

X-ray diffraction patterns of ITO films deposited by DC magnetron sputtering are presented in Fig.3. The films were annealed in air at 300℃ for 2h. The volume fraction of O_2 in the O_2/Ar mixture was 0% for curve A, 1% B, 2% C, 3% D, 4% E and 5% F. Typical peaks were assigned to the diffraction from (211), (222), (104) and (300) planes of ITO films. The spectrum at 2θ(～30 °) shows two peaks, (222) and (104), with different intensity for A, B, C, and D, but only one strong peak (222) for E and F. In addition, for A, C and D curves, the (222) diffraction is stronger than the (104) diffraction. However, for B curve, the sample not only showed that the (222) diffraction was weaker than (104), but also didn't show any (300) diffraction. X-ray diffraction experiments have provided some structural information to show the ITO films deposited with various O_2/Ar flow rate from 0% up to 5% and annealed in air at 300℃ for 2h exhibiting different resistivities and transmission described b and d curves in Fig.1. The film deposited in mixed atmosphere with O_2/Ar flow rate 1% and annealed in air at 300℃ for 2h exhibited very special resistivity and transmission.

X-ray diffraction patterns of ITO films deposited by RF method are exhibited in Fig.4. The films were also annealed in air at 300℃ for 2h. Typical peaks were assigned to the diffraction from (211), (222), (400) and (300) planes of ITO films, respectively. For all six samples, A-F, prepared with 0-5% O_2 fraction, the (222) peak is very sharp and strong. The E and F curves, the films deposited in mixed atmosphere with O_2/Ar flow rate of 4% and 5% and annealed, only show a very strong (222) diffraction peak. The difference of the shape and width of the diffraction peaks in Fig.4 in comparison with Fig.3 is remarkable. The diffraction at 2θangle of ～30 ° for the samples shown in Fig.4 appeared only one very strong sharp peak. But for the samples shown in Fig.3, the diffraction at 2θangle of ～30 ° exhibited a wide double-peaks (A, B, C, D, E curves) with different intensity and a wide single-peak (F curve). Fig.4 indicates that the films deposited by RF sputtering with post-anneal have dominant crystallization phase shown by (222) diffraction. However, the films produced by DC sputtering with post-anneal possess competitive phases shown by (222) and (104) diffraction. Therefore, the films deposited by

different sputtering (DC and RF) methods, exhibited different resistivities and transmission as seen in Fig.1 and 2.

3.3 STM imaging

Figure 5 gives STM images of ITO films deposited by DC sputtering on Si(100). The film produced in Ar atmosphere shows many domains and clear boundaries as shown in Fig.5 (a), which is in agreement with our former observation.[22] However, the films prepared in Ar and O_2 mixed atmosphere show images, Figs. 5(b)-5(f), which are different from that produced in Ar atmosphere only. As presented in Fig.6, after deposition and annealing, every sample shows a new surface topography different from the original one. STM images of ITO films deposited by RF sputtering on Si(100) are shown in Fig.7. Although the difference is only sputtering method, surface topography of the film is very different from those in Fig.5. After annealing in air at 300℃ for 2h, these surfaces changed as shown in Fig.8. For the surface topography, the changes are very complex. So, in this paper, we just show STM images. We are unable to propose reasonable interpretations.

3.4 Formation of the ITO films

In our previous work,[22] experimentally, we found that a substrate temperature of 325℃ favored of producing ITO films with lower resistivity and higher transmission. After DC magnetron sputter deposition in argon, in order to improve the electrical and optical properties, a thermal treatment (post-anneal) of the ITO films was necessary in which an annealing temperature of 300℃ and an annealing time of 2h were selected and demonstrated experimentally. Based on the results of X-ray diffraction, STM, resistivities and transmission measurements, film growth was described by two models which included amorphous film formation below a substrate temperature of 325℃(40-300℃), and crystalline film formation at a substrate temperature of 325℃ and above (325-400℃). After annealing, the amorphous films transform into crystalline films. During the formation of films, three kinds of possible nucleation sites, such as the nucleation on the substrate surface, the nucleation at the inside of the amorphous films and the nucleation at the growing surface of the films existed.[22, 27]

In this report, the substrate temperature for film deposition and the annealing temperature and time for film post-treatment are the same as those in the referenced experiments. [22] According to our previous experience, the films shown in this report should be formed in crystalline phase. The nucleation site should be on the substrate surface and at the growing surface of the films. However, because there is oxygen in the mixed atmosphere, the formation of the film has become relatively complicated. As a matter of face, the nucleation site is not only on the substrate surface and at the growing surface, but also at the inside of the amorphous films.

4. Conclusions

The ITO films were deposited by direct current (DC) and radio frequency (RF) magnetron sputtering with various parameters. Resistivity and transmission of films before and after annealing have been measured. Based on the measurement of resistivity and transmission, the films produced by DC magnetron sputtering (100W), at 325℃ substrate temperature, in an Ar and O_2 mixture containing 1% O_2 and a total pressure of ~1.7×10^{-3}Torr, show the best conductive and transparent properties without annealing. For RF magnetron sputtering (100W) , the films deposited at 325℃ with an Ar and O_2 mixture containing 3% O_2 and a total pressure of ~1.7×10^{-3}Torr, followed by annealing in air 300 ℃ for 2h, have better conductive and transparent properties.

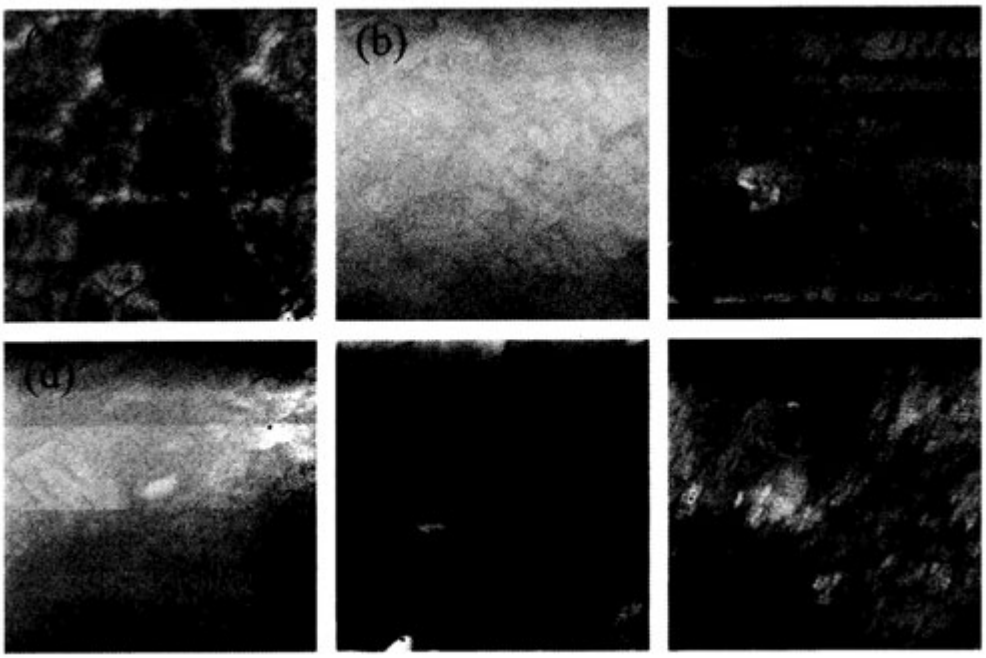

Fig.5. STM images of 100nm thick ITO films on Si(100), scan size is $498\times498nm^2$, sample bias voltage V is 1.40V and tunneling current I_t is 0.06nA for (a) and (c), 0.05nA for (b), (d), (e) and (f). The films were deposited by DC 100W, at substrate temperature 325℃, under Ar and O_2 mixed pressure of ~1.7×10^{-3}Torr in which O_2/Ar flow rate was 0%(a), 1%(b),2%(c), 3%(d), 4%(e) and 5%(f).

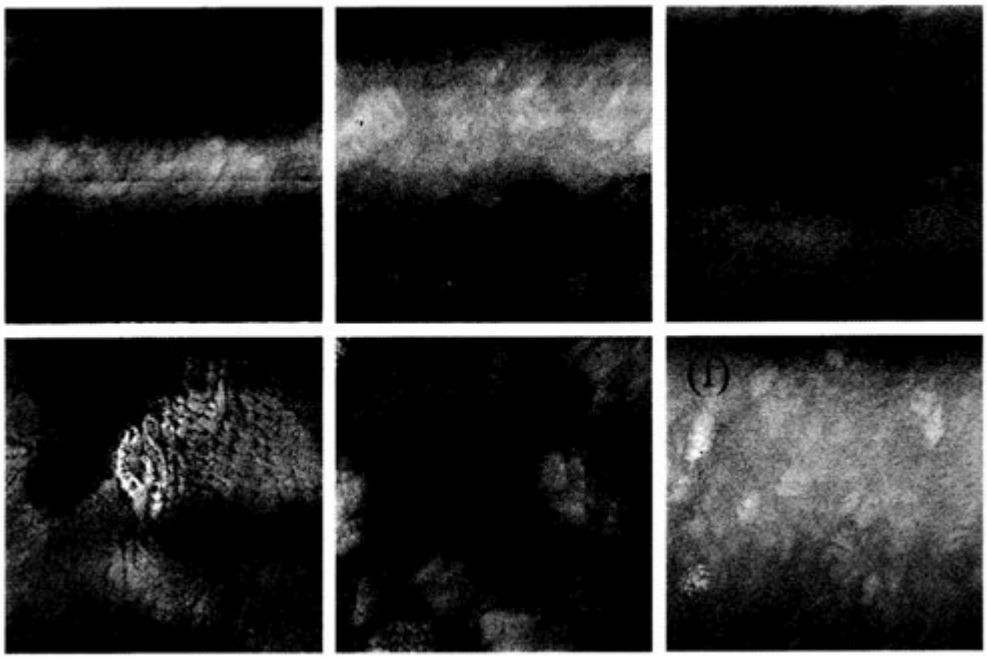

Fig. 6. STM images of 100nm thick ITO films on Si(100) after deposition, and annealing in air at 300℃ for 2h, scan size is 498×498nm^2, sample bias voltage V is 1.40V and tunneling current I_t is 0.06nA for (a) (e), 0.04nA for (b), (c), (d) and (f). The films were deposited by DC 100W, at substrate temperature 325℃, under Ar and O_2 mixed pressure of ~1.7×10^{-3}Torr in which O_2/Ar flow rate was 0%(a), 1%(b),2%(c), 3%(d), 4%(e) and 5%(f).

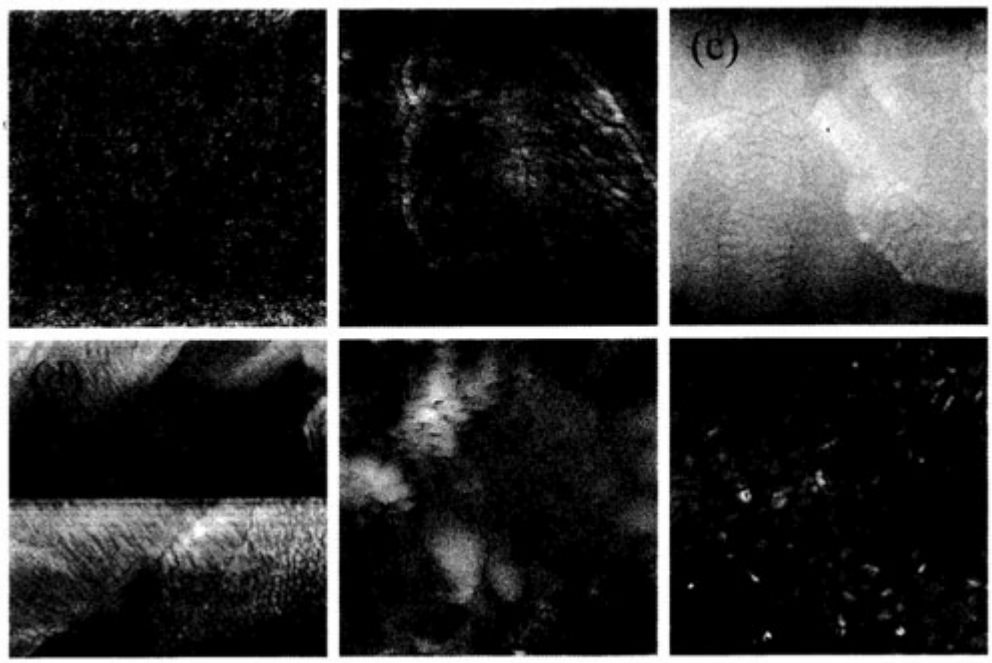

Fig.7. STM images of 100nm thick ITO films on Si (100), scan size is 498×498nm^2, sample bias voltage V is 1.40V and tunneling current I_t is 0.03nA for (a), (b), (d) and (f), 0.02nA for (c) and 0.04nA for (e). The films were deposited by RF 100W, at substrate temperature 325 °, under Ar and O_2 mixed pressure of ~1.7×10^{-3}Torr in which O_2/Ar flow rate was 0% (a), 1%(b), 2%(c), 3% (d), 4% (e) and 5% (f).

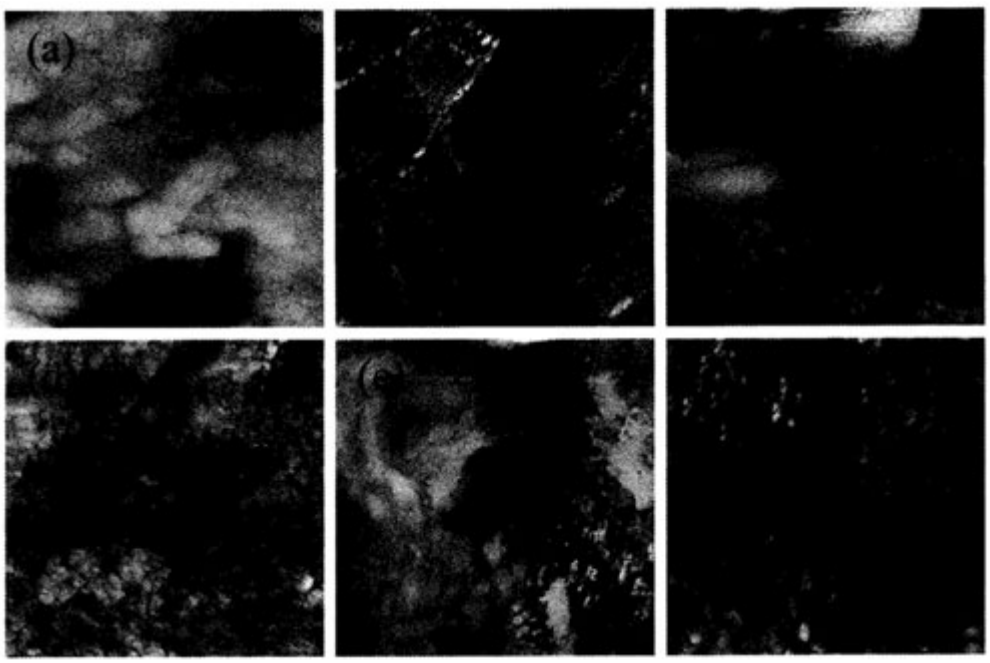

Fig.8. STM images of 100nm thick ITO films on Si (100) after deposition and annealing in air at 300℃ for 2h, scan size is 498×498nm^2, sample bias voltage V is 1.40V and tunneling current I_t is 0.03nA. The films were deposited by RF 100W, at substrate temperature 325 ° , under Ar and O_2 mixed pressure of ～1.7×10^{-3}Torr in which O_2/Ar flow rate was 0% (a), 1% (b), 2% (c), 3% (d) , 4%(e) and 5% (f).

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