Indium tin oxide films with low resistivity and low internal stress

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Indium tin oxide (ITO) films prepared by dc magnetron sputtering were annealed in air, vacuum, and oxygen gas atmospheres. The electrical properties and internal stresses of these annealed ITO films were systematically investigated. It was found that, among the above postannealing treatments, oxygen gas annealing significantly reduced both the resistivity and the internal stress in ITO films at fairly low temperatures of 100–150 °C. Resistivities and internal stresses as low as $7 \times 10^{-4}\ \Omega$ cm and 38 MPa, respectively, were obtained by annealing in oxygen gas atmosphere at 100 °C. It was also revealed that the (111) crystal orientation becomes dominant and that whole grains grow dramatically as a result of postoxygen annealing, even at 100 °C. [DOI: 10.1116/1.1563623]

I. INTRODUCTION

Indium tin oxide (ITO) is widely used to make a transparent conducting film for various display devices. These ITO films are conventionally deposited on a glass substrate, but deposition on a polymer substrate has recently received considerable attention for use in future display applications. To achieve this, ITO films with low resistivity, low internal stresses, and high optical transmittance are required in relatively low-temperature processes. Many processing studies of ITO films have been conducted with the aim of obtaining films with both low resistivity and high optical transmittance.[1–4] It has been reported that ITO films with either low resistivity or low internal stress can be obtained by either optimizing substrate temperatures during sputtering or postannealing in air.[2] However, to my knowledge, there are few reports of ITO films with both low resistivity and low internal stress having been successfully obtained in relatively low-temperature processes at less than 200 °C.

For this purpose, an investigation was undertaken to determine the effects of annealing ITO films in various gas atmospheres, such as vacuum, air, and oxygen gas. As a result, it was found that ITO films satisfying the above requirements can be obtained by heat treatment in oxygen gas atmosphere.

II. EXPERIMENT

ITO films (260–280 nm in thickness) were prepared by dc magnetron sputtering on a glass substrate at room temperature. The target used was a sintered ceramic target with a mixture of 95 wt % In_2O_3 and 5 wt % SnO_2. The sputtering was performed using a high purity Ar+2 vol % O_2 gas mixture (99.999%) whose total pressure was kept at 0.7 Pa during deposition. The structure of all the present as-deposited ITO films was not amorphous, but polycrystalline as mentioned below. The resistivity and electron mobility of the films before and after annealing were measured by Hall effect measurements using the Van der Pauw method at room temperature. The film surface morphology was observed with atomic force microscope (AFM, Epson SPI3800N), and the structure and the internal stress were investigated and measured, respectively, by using thin-film x-ray diffractometer (Rigaku RINT 2500). As-deposited films were annealed at temperatures between 100 and 300 °C in (1) a vacuum (less than 10^{-3} Pa), (2) air, and (3) a gas flow of pure oxygen.

The composition of as-deposited films measured qualitatively by using an x-ray fluorescence analysis (Rigaku RIX2500) was 95–96 wt % In_2O_3 and 4–5 wt % SnO_2, almost the same as the target composition used in the present sputtering.

III. RESULTS AND DISCUSSION

Figure 1 shows the changes in resistivity, electron carrier density, and Hall mobility for ITO films annealed in a vacuum, air, and flow oxygen gas, respectively, at each temperature for 30 min. It should be noticed that for the oxygen-annealed samples, the resistivity decreased markedly from 57×10^{-4} to $7\times10^{-4}\ \Omega$ cm at 100 °C, and showed low values of $5\times10^{-4}\ \Omega$ cm at 200 °C, and then tended to increase with annealing above 250 °C. In contrast, the resistivity of both vacuum- and air-annealed samples monotonically decreased with increasing annealing temperatures, and reached values as low as $4\times10^{-4}\ \Omega$ cm above 250 °C. On the whole, the mobility of different annealing samples increases monotonically with the annealing temperatures. However, the dependence of carrier density on annealing temperature is quite different for each sample, depending on different heat treatments used. It was revealed that the carrier density of oxygen-annealed samples increases markedly at 100 °C and then decreases above 200 °C, while those of vacuum- and air-annealed samples start to increase above 200 and 250 °C, respectively. The general tendency of the change in carrier density appears to be opposite to that of the change in resis-

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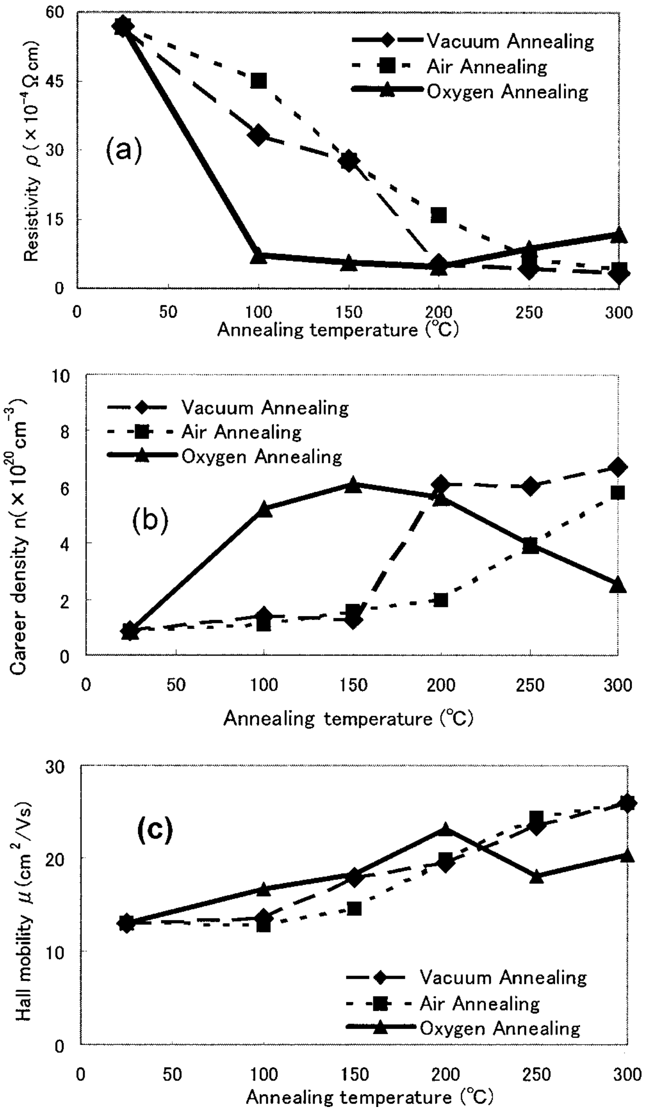

FIG. 1. (a) Resistivity ρ, (b) carrier density n, and (c) Hall mobility μ of the ITO films annealed in various gas atmospheres as functions of the annealing temperatures.

tivity. Thus, the main cause of the change in resistivity is most likely due to the change in carrier density in films annealed using various heat treatments.

Figure 2 shows the change in Internal stress as a function of the annealing temperature for samples annealed by using various heat treatments. All of the internal stresses measured were compression. Note that the internal stresses of oxygen-annealed samples decrease sharply from 1400 to 38 MPa in compression mode at 100 °C and show almost constant low values with further increases in the annealing temperature. In the case of vacuum annealing, the internal stresses start to decrease markedly at 200 °C and show almost constant values ($\sim$100 MPa) with further increases in the annealing temperature. On the other hand, those of air-annealed samples do not change significantly within the range of the present annealing temperatures, and show relatively high compression values (about 1100 MPa). These results indicate that internal stresses in ITO films can be largely reduced at relatively low

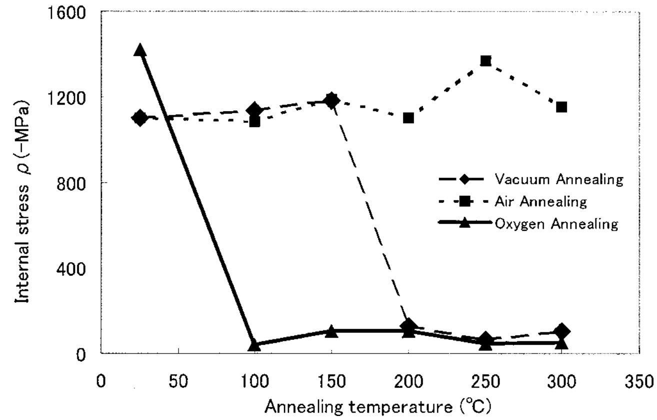

FIG. 2. Change of internal stress in ITO films annealed in various gas atmosphere as functions of the annealing temperature.

temperatures by annealing them in oxygen gas atmosphere.

The changes in the surface morphologies of ITO films annealed, respectively, at 100, 200, and 300 °C in various gas atmospheres were observed with AFM, and are shown in Figs. 3–5. In Fig. 3, the surface morphology of as-deposited ITO films is also included as a reference. Note that particularly large grain growth has already taken place for the samples annealed at 100 °C in the oxygen atmosphere [Fig. 3(d)], which is quite different from the results for samples annealed in either air [Fig. 3(c)] or vacuum [Fig. 3(b)]. Such recrystallized grain sizes do not significantly change with further high temperature annealing (see Figs. 4 and 5). In the case of samples annealed in vacuum, a large grain growth starts to occur at 200 °C as shown in Fig. 4(a) and their grain sizes are also nearly unchanged with further high temperature annealing at 300 °C as demonstrated in Fig. 5(a). On the other hand, samples annealed in air do not show a large grain growth even with high temperature annealing as shown in Figs. 4(b) and 5(b). Since a large grain growth due to recrys-

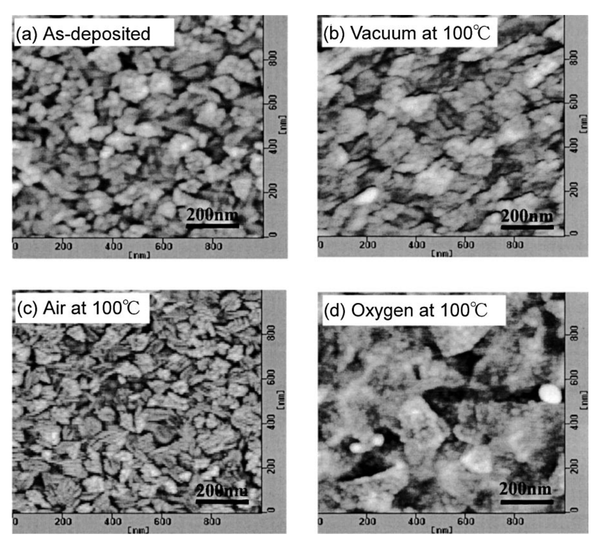

FIG. 3. AFM images of surface morphologies of the ITO films before annealing (a) and after annealing at 100 °C in (b) vacuum, (c) air, and (d) oxygen atmosphere.

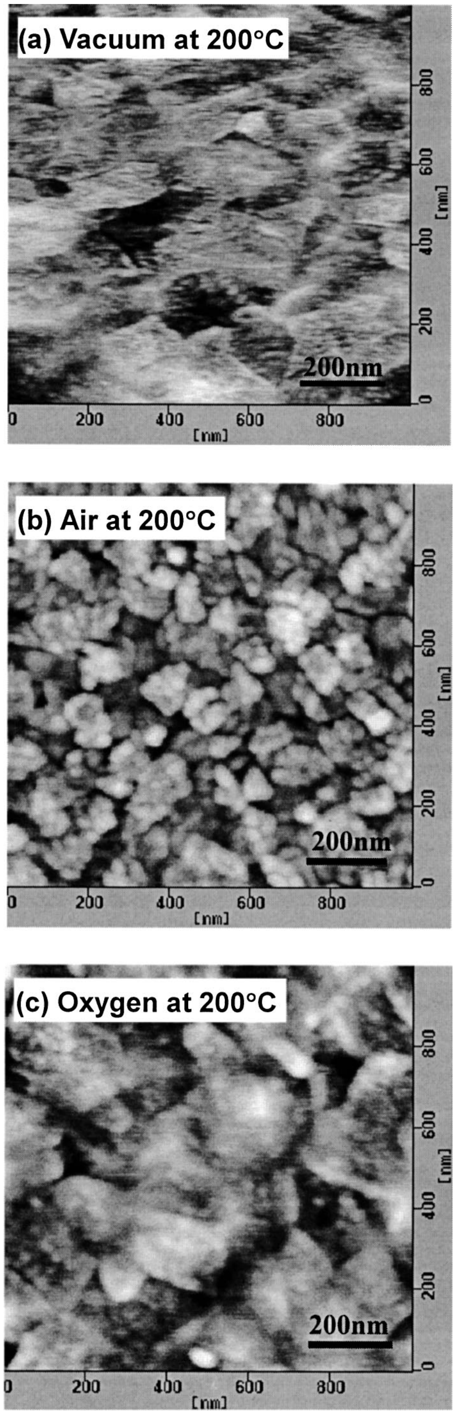

FIG. 4. AFM images of surface morphologies of the ITO films after annealing at 200 °C in (a) vacuum, (b) air, and (c) oxygen atmosphere.

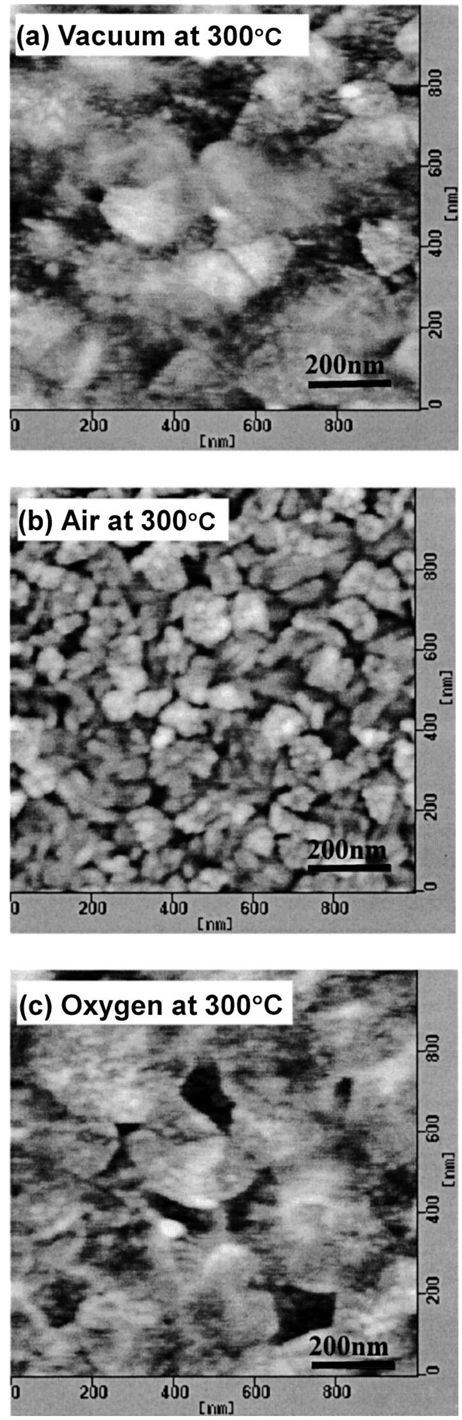

FIG. 5. AFM images of surface morphologies of the ITO films after annealing at 300 °C in (a) vacuum, (b) air, and (c) oxygen atmosphere.

tallization usually causes a large stress relief, the large increase in grain size for the samples annealed in oxygen or vacuum atmosphere most likely plays a large role in reducing the internal stress significantly at low temperatures. Particulary, oxygen annealing can enhance low temperature recrystallization accompanied by a large internal stress relief in ITO films.

It is well known that ITO films are categorized as *n*-type semiconductors. Their free electrons arise from oxygen vacancies or tin ions on substitutional sites of indium ions.[5] Therefore, resistivities are expected to be increased by filling of oxygen vacancies through penetration of oxygen in the ITO films. Indeed, the resistivity and electron carrier density of the present as-deposited ITO films increase and decrease, respectively, with increasing an oxygen admixture to the Ar sputtering gas during sputtering. However, this is not consistent with the result of a large decrease in resistivity accompanied by a large increase in carrier density for the samples

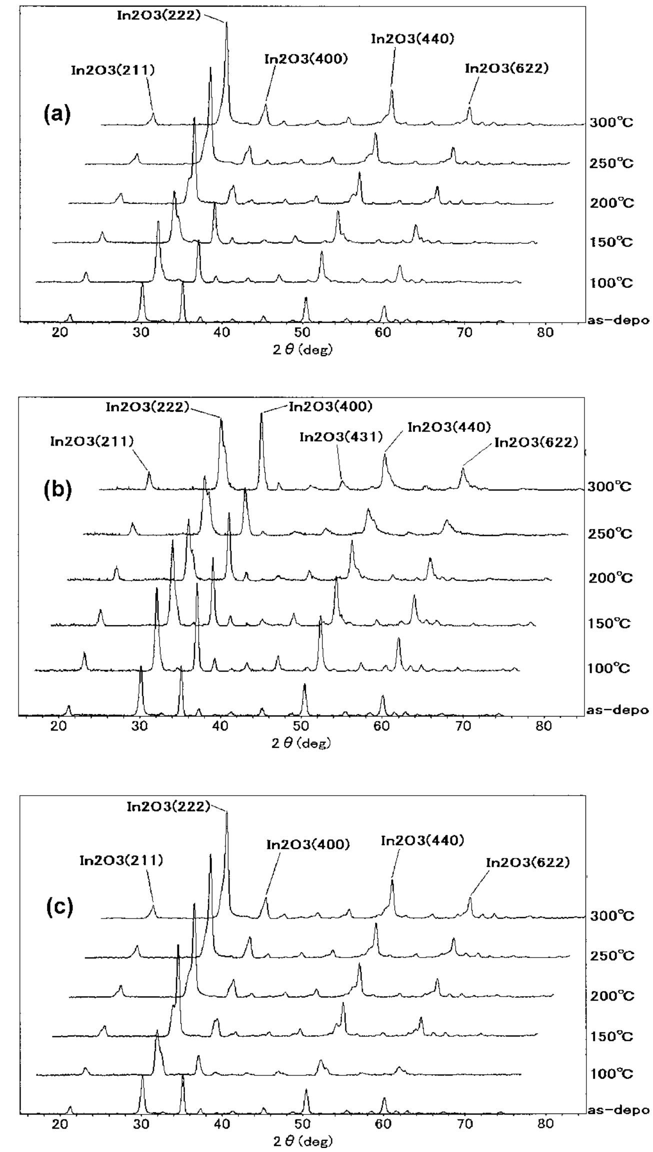

FIG. 6. X-ray diffraction profiles of the samples annealed in (a) vacuum, (b) air, and (c) oxygen gas atmosphere at various annealing temperatures.

annealed in oxygen gas atmosphere at 100–200 °C. Since the above large grain growth can also cause less grain boundary scattering for carrier free electrons in the films, the latter can be attributed partly to an increase in carrier electron concentration resulting in a large decrease in resistivity, as shown in Figs. 1(a) and 1(b). The increase in resistivity associated with the decrease in carrier density for the films annealed in oxygen gas atmosphere above 200 °C most likely results from filling of oxygen vacancies by absorption of oxygen into the films during oxygen annealing.

Representative x-ray diffraction profiles of samples annealed in a flow oxygen gas, vacuum and air at various annealing temperatures are presented, respectively, in Figs. 6(a)–6(c). Temperatures listed at the right hand side of the figures indicate the postannealing temperatures employed. Note that the present as-deposited films (as-depo in the figures) are not amorphous, but a crystalline structure with two strong (222) and (400) crystal orientations. Comparing with Figs. 1 and 2, the (400) diffraction intensity significantly decreases accompanied by the large increase of the (222) intensity when both resistivities and internal stresses largely decrease on annealing. This indicates that a preferential crystal growth toward the (222) orientation takes place when the grain size becomes extremely coarse. This (222) type of preferred orientation, however, does not always yield a decrease in both resistivities and internal stresses of ITO films, though the addition of oxygen to Ar in sputtering also enhances the crystallization of films.[3,4] Indeed, present samples prepared by addition of more than 10% oxygen to the sputter Ar during sputtering show a strong (222) intensity compared with the (400) one. These as-made films prepared in high oxygen content in the sputter Ar show very high resistivities of more than 100 Ω cm. Note that x-ray diffraction profiles in air atmosphere do not significantly change with annealing. These results are quite different from other atmospheric annealing. In particular, the peak of $In_2O_3(400)$ does not apparently decrease with increase of annealing temperature, indicating that present as-made ITO samples do not show a large structure change in air annealing. These facts are also revealed by the results of no significant grain growth in air annealing as compared with Figs. 3(a) and 5(b). Judging from the above results, the recrystallization of ITO films in postannealing most likely largely depends on both oxygen content in an annealing atmosphere and as-made structures of ITO films. Note that amorphous ITO samples do not show the significant improvement of resistivities and internal stresses at 100 °C in oxygen annealing, though depending on conditions of sample preparation, which will be reported elsewhere. The mechanism of the effects of oxygen on the recrystallization of ITO films is still not clear and left for further future work.

Finally, the optical transmittance of all of the postannealed films in oxygen gas atmosphere was measured and found to be more than 90% in the visible region of the solar spectrum.

IV. SUMMARY

Indium tin oxide (ITO) films prepared by dc magnetron sputtering were annealed in air, vacuum, and oxygen gas atmosphere. It was found that, among the above postannealing treatments, oxygen gas annealing significantly reduced both the resistivity and the internal stress in ITO films at fairly low temperatures of 100–150 °C. Resistivities and internal stresses as low as 7×10^{-4} Ω cm and 38 MPa, respectively, were obtained by annealing in oxygen gas atmosphere at 100 °C. It was also revealed that the (111) crystal orientation becomes dominant and that whole grains grow dramatically as a result of postoxygen annealing, even at 100 °C.

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