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논 문
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산화물 Target의 RF 마그네트론 스파터링에 의한 비손상 SnO_2 박막의 제조

Preparation of Damage-less SnO_2 Thin Films by RF Magnetron Sputtering with Oxide Target

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요 약

RF 마그네트론 스파터링에 의한 SnO_2 박막을 증착한 결과 작동조건에 따라 표면에서 막손상이 발생하였는데, 이는 target에서 생성된 높은 에너지의 고속입자가 기판에서 직접 충돌로 일어나며, 마그네트론의 자계분포와도 관계된다. 또한 기판의 위치에 따라 박막의 전기적, 구조적 특성이 급격히 변하는데, 본 논문은 중심자석의 세기와 RF power, 가스압력, 그리고 기판온도 등의 스파터링 작동조건을 변화시키면서 박막의 비손상을 검토하였고, 물성 특성을 평가하였다. 실험결과로 부터 기판의 외측부에서 제작된 박막은 전반적으로 막손상이 없었고, 특히 target의 중심자석을 Cobalt로 설치하고 15 mTorr의 가스압력과 50 W의 RF power로 한 경우 가장 우수한 특성을 가진 박막을 얻을 수 있었다. 추가로 막손상을 방지하고자, 환원형의 masking glass를 target위에 설치하였는데, 고에너지 입자의 직접 충돌을 확실히 차단할 수 있었으며, 비저항율도 target의 부식부위 (erosion)에 대응하는 부분에서 100배 정도로 개선하였다.

Key Words (중요용어) : RF magnetron sputtering, SnO_2, surface damage (막손상), Resistivity (비저항), Masking glass (차단유리)

1. Introduction

Transparent and conducting films such as SnO_2, ITO and ZnO are significant for applications of solar cell, optoelectronic device, and heat mirrors, etc. However, there are severe restrictions on structural damage, thickness uniformity, optical transparency and electrical conductivity of the transparent electrode films used in such devices. A magnetron sputtering system, offering high deposition rate at low pressure and onto large-area substrates as well, is important method with the preparation of transparent and conducting films in both research and industrial fields.

In normal operation of the balanced magnetron sputtering, the majority of electrons in the plasma is confined to a dense horizontal magnetic field in the vicinity of target surface. By changing the configuration of this horizontal magnetic field towards the vertical one, the number of electrons bombarding the substrate can be controlled. The variation on the condition of electron bombardment, which is necessarily accompanied by the ion bombardment during the growth of thin films, produces the immense changes in the film properties: that is, film stress[1,2] optical properties[3,4] electrical properties and morphology[5] for the cases of metal, compound oxides, and nitride. Window et al[1,4] using Langmuir probe, clarified that the relation between the change of magnetic distribution and the change of self bias was caused by electron bombardment onto the substrate.

Apart from electron bombardment, the neutral

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sputtered gas atoms with high-energy, which were bounded out of the target surface and bombarded onto the substrate in a typical sputtering technology for metals and compound oxides deposition, were observed by Nakazama et al.[5,6,7] They explained that the elevated resistivity at the position on the deposited ZnO film facing to the erosion region of target was obviously produced by the high-energy neutral sputtered gas atoms as a result of the bombardment on film surface. However, the energy of these particles was, of course, not so sufficient (about 10~15 eV) as to damage the films. Tominaga et al.[6] confirmed that the energetic negative oxygen ions and the neutral oxygen atoms were originated by the negative oxygen ions (about 350 eV) in terms of the time-of-flight method in the sputtered ZnO and $BaTiO_3$.[8] They determined that the structural degradation of oxygen films at the position facing to target erosion was occurred by the bombardment of energetic negative oxygen ions and oxygen atoms.

SnO_2 electrode films are developed for a solar cell using a RF magnetron sputtering system. It is well known that the characteristics of as-deposited film are significantly influenced the bombardment of high-energy particles concentrated at the erosion region of target as well as the configuration of magnetic field near the target. In this paper, the details of those effects for the SnO_2 films using a rf magnetron sputtering method are discussed. In order to prevent the non-uniform distribution of electrical resistivity on the film surface caused by the bombardment of incident high-energy particles, there is an attempt using a ring plate of masking glass.

2. Experimental details

SnO_2 films were prepared on the soda lime glass($26 \times 76 \times 1mm^3$) by a RF magnetron sputtering system under Ar atmosphere. Target material was mounted onto a water cooled cathode with a permanent magnet assembly. The center magnet under the target could be replaced to another type of magnet to control the strength and direction of magnetic field as shown in Fig. 1. The target was a hot-pressed SnO_2 (99.99% pure) disk (100 mm in diameter and 5 mm in thickness), supplied by Furuchi Chemical Corporation. The target-substrate distance was fixed by 4 cm. The operating pressure of Ar gas (99.9999 %) varied from 5×10^{-3} to 3×10^{-2} Torr. The target was pre-sputtered in pure Ar gas at a pressure of 1×10^{-2} Torr for 10 min. to remove the absorbed water and contamination layer on the target surface. The RF power was controlled from 30 W to 60 W. A ring plate of masking glass was installed at the 1.5 cm distance above the target and faced to erosion region of the target to investigate the effect of direct bombardment on SnO_2 film surface by high-energy particles.

The film thickness was measured by a surface roughness detector with a stylus (ET-10, Kosaka Laboratory Co.). The electrical resistivity of the as deposited films was estimated by four probe method with a dc power supply (PAB18-3A, Kikusui Co.), two kinds of digital multimeters (CDA-701, Sanwa Co., and R6341A, Advantest Co.) and a four probe electrode (Kullicke & Soffa Co.). The crystal structure of the SnO_2 films was plotted with X-ray diffraction apparatus (Rotaflx, RigaKu Co.).

3. Results and Discussion

3.1 Influence of magnetic field distribution

Fig. 1 shows a RF magnetron sputtering system including a target assembly which a center magnet is mounted or does not exist. When Co (Cobalt) magnet exists in the target center, electrons are confined to the horizontal magnetic field in the vicinity of the target, so that only few electrons reach to the substrate. With a decrease of magnetic pole strength in the center magnet, the magnetic field diverges towards the substrate along the vertical component of magnetic field lines and the electrons become also to diverge towards the substrate. The electron bombardment makes the substrate to be self-biased negatively, and positive ions begin bombarding the substrate which neutralizes the bias potential.[1,4,9]

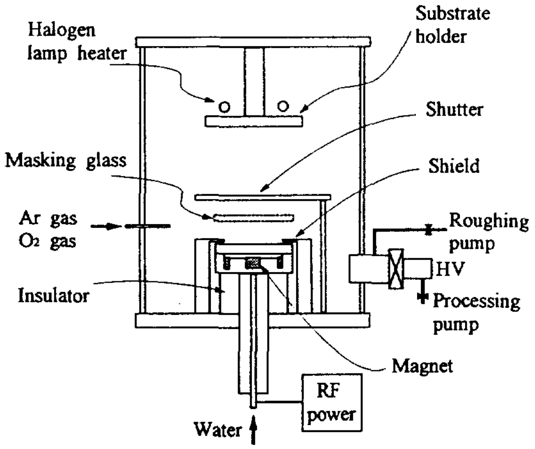

Fig. 1. Schematic diagrams of RF magnetron sputtering system including target assembly.

There are three types of center magnet to deposit the SnO_2 thin films; that is, Co, Fe (Ferrite) magnet and no center magnet. The magnetic field strength of Fe magnet, which is practically measured at several points of space above the target surface, is a little weaker than that of Co magnet, in spite of large difference of magnetic pole strength between Co (8000 gauss) and Fe (2000 gauss) magnets. The distribution of magnetic field is the intermediate state whichever types of the center magnet exist. Fig. 2 shows the deposition rates of SnO_2 thin films with the variations of center magnet type. It expresses that the deposition rate depends completely upon the magnetic pole strength of center magnet.

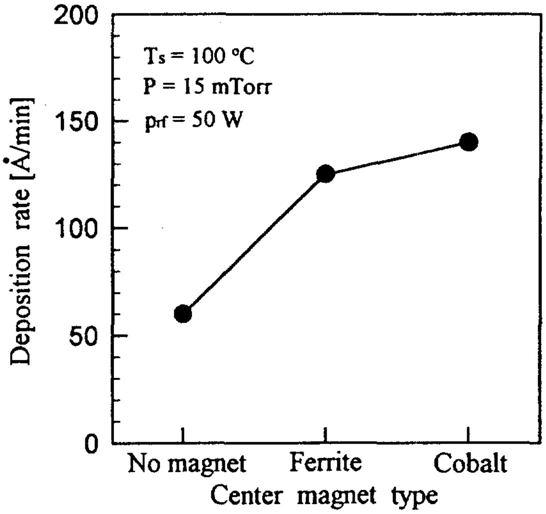

Fig. 2. Deposition rate of SnO_2 thin films with center magnet type at the center location of substrate.

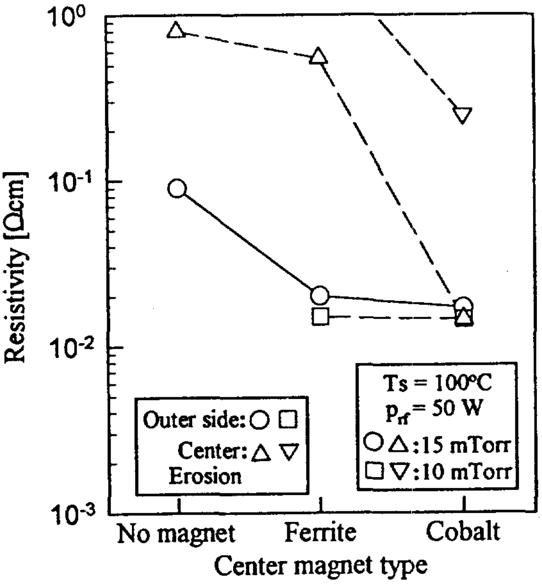

Fig. 3. Resistivity of SnO_2 films with center magnet type at several location of substrate.

Fig. 3 shows a plot of the electrical resistivity with the center magnet at the different position of substrate. In the case of Co magnet, the resistivity at the outer side position of substrate does not change for the two gas pressures of 10 mTorr and 15 mTorr. But the resistivity of substrate center and location facing to the erosion positions on target at the pressure of 10 mTorr is about 10 times as large as the value at 15 mTorr. When the films are prepared by a magnetron sputtering with Fe center magnet, the resistivity at the outer side of substrate is almost same value with the film prepared by Co center magnet. However, the resistivity of center position is larger about 10 times than that of the film prepared with Co magnet at 15 mTorr.

Fig. 4 shows the surface profile of as-deposited SnO_2 films with the various damage states. The film surface at the center position with Cobalt magnet at 10 mTorr and with Fe magnet at 15 mTorr are partially damaged as shown in Fig. 4(b). The film surface at the center position prepared with Fe magnet at 10 mTorr is completely damaged as shown in Fig. 4(c), so that the resistivity of the film is not able to detect. When the center magnet does not exist, the film is not damaged and the electrical resistivity of film at the center and outer side position is, however, higher than that with Cobalt and Fe magnet at 15 mTorr as shown in Fig. 3. Furthermore, the plasma state is unstable to prepare the film at 10 mTorr.

The crystallinity patterns with different location of the as deposited films as a function of various center magnets and sputtering gas pressures are shown in Fig. 5. When the center magnet does not exist, the characteristic peaks in X-ray diffraction pattern of SnO_2 show slightly up and, however, not well developed as shown in Fig. 5(a). The film surface is not damaged state at both locations of center and outer side location. In the case of Fe magnet as shown in Fig. 5(b), the peak intensity of SnO_2 film deposited at substrate center is lower than that of the outer side position because the film is partially damaged such as shown in Fig. 4(b). In the case of Co magnet (c), the peak intensity at the center and position facing to the erosion on target is well developed than the outer side location. Their film surface is also not damaged and shows clear state. When the sputtering gas pressure is 5 mTorr in Fig. 5(d), the main peaks of film at the outer side are well developed in the <101> direction.

But the film surface in location facing to the erosion target is completely damaged as shown in Fig. 4(c) and its characteristic peaks are not observed clearly as shown in Fig. 5(d). Tominaga et al.[8,9] also observed such damage phenomena on the as-deposited ZnO film facing to the erosion position of a ZnO target and disappearance of the characteristic peak of ZnO at low sputtering gas pressures.[10] They detected high-energy (350 eV) oxygen ions and oxygen atoms by the time-of-flight method as well as explained their influence on film properties through direct bombardment phenomenon.

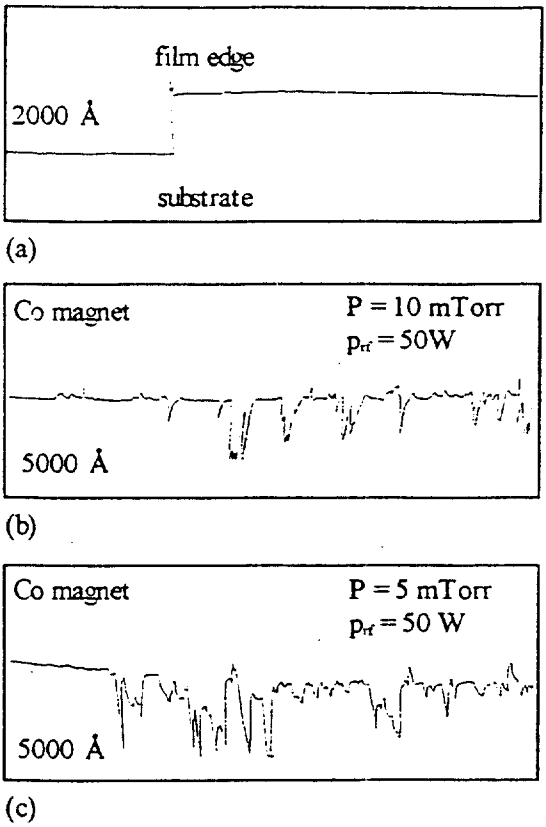

Fig. 4. Surface profiles of SnO_2 films at various surface damages:
(a) No damage
(b) Partial damage (mainly at center position in Co magnet at 10 mTorr and Fe magnet at 15 mTorr for RF power of 50 W)
(c) Complete damage (mainly at center position in Co magnet at 5 mTorr and Fe magnet at 10 mTorr for RF power of 50 W)

The magnetic field distribution above target surface and the bombardment strength of high-energy particles from the target influences for the film properties with different location on the substrate. Total bombardment strength is different with the kinds of center magnet as fellows. In the case of Co center magnet, the

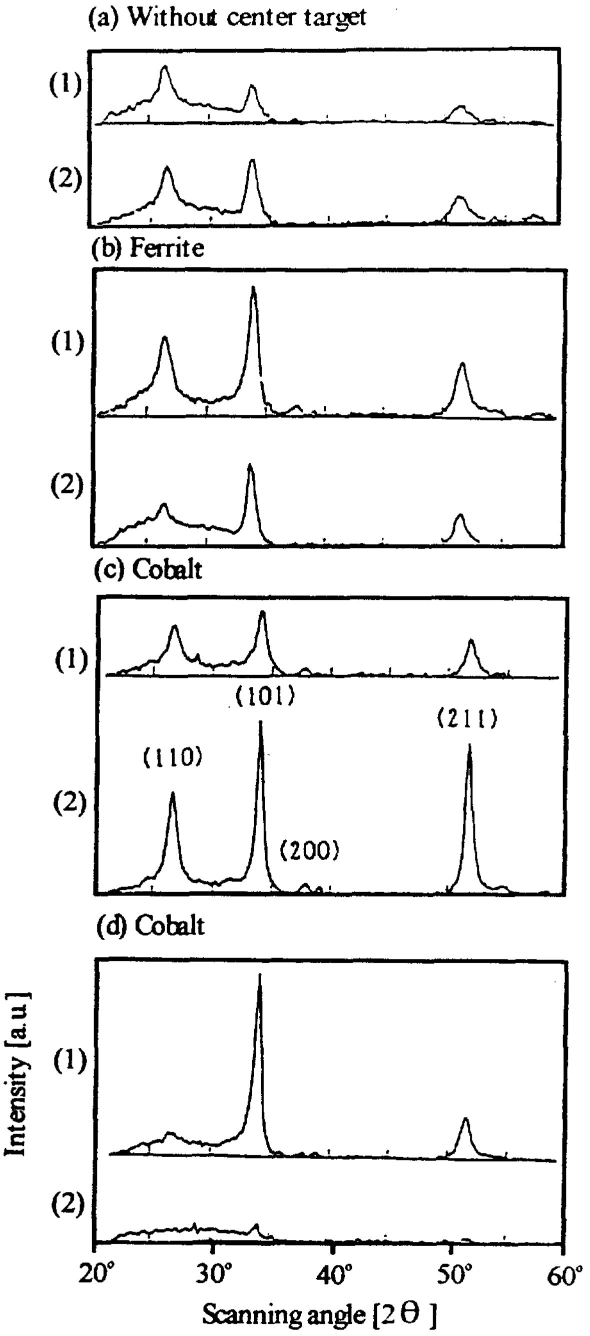

Fig. 5. X-ray diffraction patterns of SnO_2 films at (1) outer side and (2) center of substrate
Sputtering conditions: Ts = 100℃, P = 15 mTorr, P_{rf} = 50 W→ (a), (b), (c)
Ts = 100℃, P = 5 mTorr, P_{rf} = 50 W →(d)

bombardment strength of high-energy oxygen ions and neutral atoms is stronger than that of Fe magnet. Although the high-energy particle bombardment at low gas pressure is a serious problem occurring damage on the film surface, the crystallinity at high sputtering gas pressure of 15 mTorr as shown in Fig. 5(c) is oriented enough. As the center is Fe magnet, a part of the magnetic field lines in the outer Co magnet diverges vertically, and penetrates the substrate. Thus, the electrons and ions, which are led by the penetrating magnetic field, become to bombard the substrate. Total bombardment strength is now sufficient to damage the film. The penetrating magnetic field becomes larger than that of the case without center magnet, but the high-energy bombardment is smaller due to the low plasma density in the vicinity of the target. Consequently, total bombardment strength is not sufficient to damage the film and not help the development of crystallinity.

Although the magnetic field distribution is not affected at all by the decrease of sputtering gas pressure, the bombardment of high-energy particles is enhanced with lengthening the mean free path of the particles at low gas pressure. Window[11] mentioned that the film properties in center and erosion location of substrate were dominated by the magnetic field effect in the unbalanced magnetron system, and the number of bombarding high-energy particles was closely related to the plasma density. Therefore, the film position facing to the erosion position of target is more damaged than the other position of substrate.

3.2. Influence of RF power and sputtering gas pressure

Fig. 6 shows the variations of deposition rate as a function of sputtering gas pressure with the various positions of substrate at RF powers of 30 and 50 W. The deposition rate obviously increases with the increase of RF power and decreases with the decrease of sputtering gas pressure. The box in Fig. 6 indicates that the film surface is partially or completely damaged.

Fig. 7 shows the electrical resistivity as a

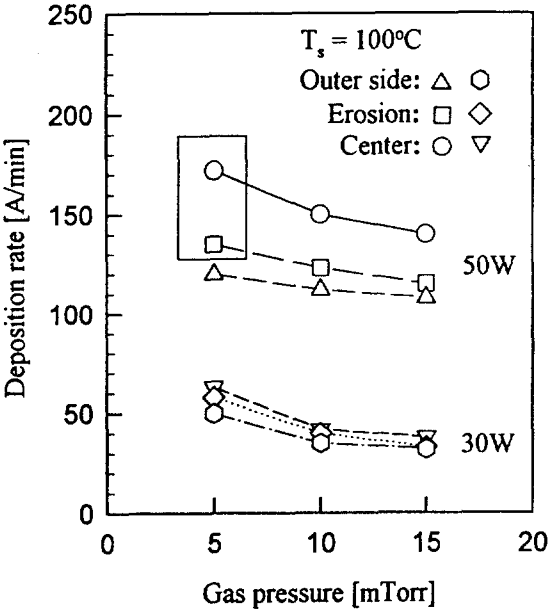

Fig. 6. Deposition rate of SnO_2 films as a function of Ar gas pressure at several locations of substrate.

function of RF power with the different sputtering gas pressure. The resistivity on the outer side of film is gradually decreases in proportion to the increase of RF power in 15 mTorr as shown in (a). The resistivity of substrate center and location facing to the erosion on target decreases with increase of RF power below 50 W, and is, however, rapidly increased above 50 W. But their film surfaces are partially damaged as shown in part A of Fig. 7. With the decrease of sputtering gas pressure and the increase of RF power as shown in Fig. 7, the resistivity of center and location facing to the erosion on target increases. The films generate even a partial damage at the lower values of RF power (part B and D) and the damage on film surface is more intensified with decreasing sputtering gas pressures at the same RF power.

Fig. 8 shows the variations of electrical resistivity for the changes of RF power and sputtering gas pressure only at the location facing to the erosion on target. The points in the triangle region of part F indicate that the film surface has a damage. The as-deposited films without damage are able to prepare at low

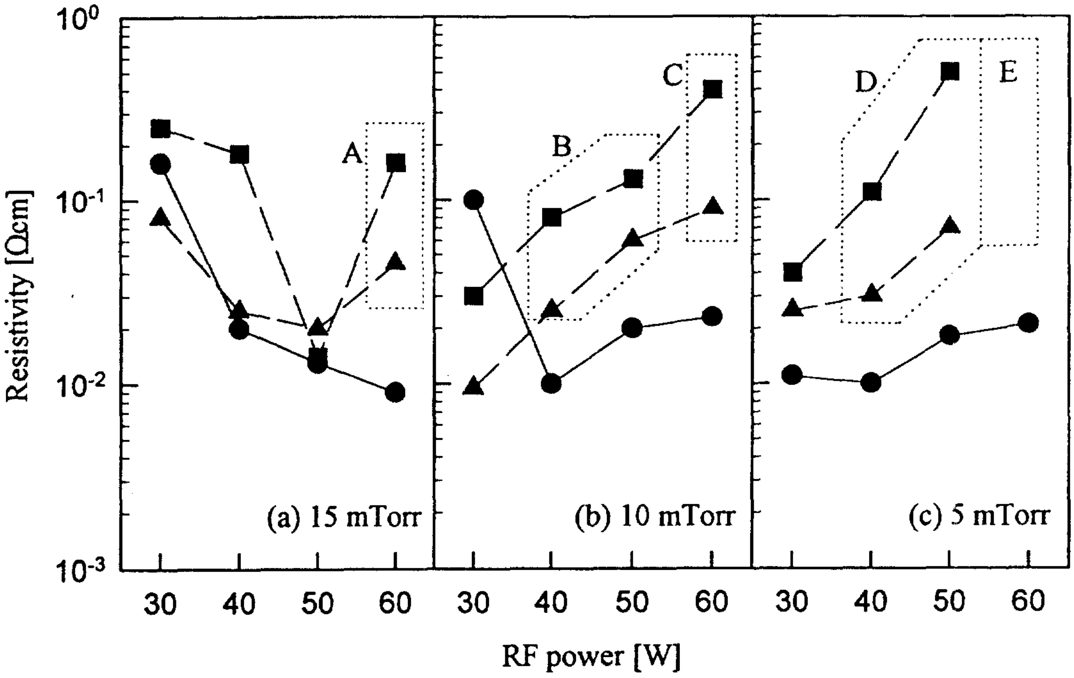

Fig. 7. Resistivity of SnO_2 films as a function of RF power in several substrate locations at substrate temperature of 100℃; partial damage: A and B, more damage: C and D, complete damage: E. (symbols; outer side: ● , erosion: ■ , center: ▲)

RF power under low sputtering gas pressure as well as at high RF power under high gas pressure over 10 mTorr as shown in Fig. 8. But the resistivity with various location is different from the above results under the same conditions, due to the difference of the bombarding energy in particles. The film, which has the lowest resistivity and the most uniform surface, is prepared only under the RF power of 50 W and the sputtering gas pressure of 15 mTorr as shown in Fig. 8..

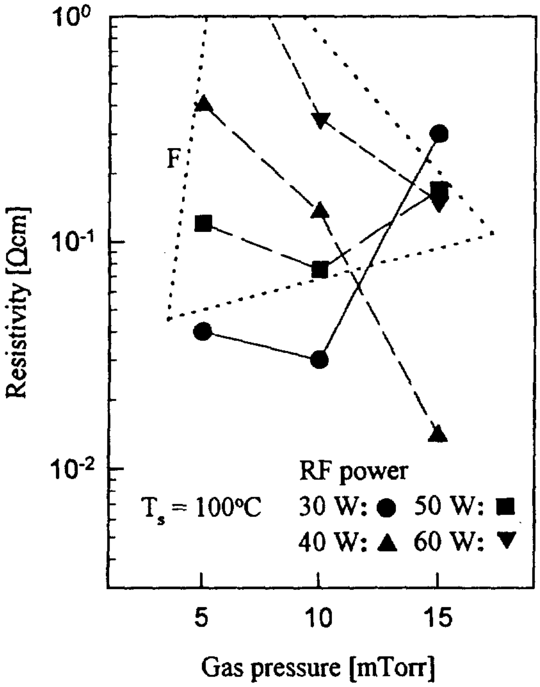

Fig. 8. Resistivity of SnO_2 films as a function of Ar gas pressure at substrate location facing to target erosion (damaged zone: F)

3.3 Influence of masking glass

In order to observe the direct bombardment of high-energy oxygen ions and neutralized atoms confined above the erosion position of target, a ring plate of masking glass is mounted at 1.5 cm above the target surface. The effect of masking glass is obviously shown in Fig. 9. Therefore, the direct bombardment of energetic particles into the substrate is able to prevent. The resistivity in the position facing to erosion region on substrate is decreased by almost 100 times as shown in Figure, as well as that of substrate center is also decreased steeply. It is sure that the uniform and low resistivity films is prepared by the installation of masking glass at low sputtering gas pressure. But the deposition rate is reduced less about half than that of the film prepared without masking glass under the same operating condition.

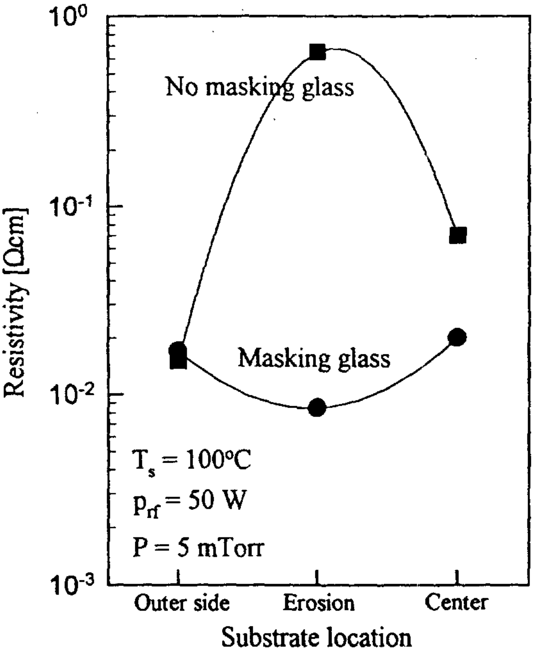

Fig. 9. Resistivity of SnO_2 films for substrate locations with/without masking glass.

4. Conclusions

The magnetic field distribution above target surface influences directly on the bombardment of high-energy particles bounded out of the target. The electrical and morphological properties of as-deposited SnO_2 films are investigated by the magnetic field, RF power, and operating gas pressure. The film properties depend obviously on the total bombardment strength which is a sum of the bombardment of electrons and ions induced by the magnetic field effect and the bombardment of high-energy particles bounded out of the erosion position of target. When the center magnet is Ferrite, the film is more damaged by synergistic effect of magnetic field and particle bombardment at pressure of 10~15 mTorr and RF power of 50 W. In the case of Co center magnet, film is mainly damaged by the direct bombardment of high-energy particles at RF power of 50 W and below gas pressure of 10 mTorr.

However, it is sure that the increasing sputtering gas pressure disperses effectively the high-energy particles from the oxide target and reduces the electrical properties and damages in the different position of as-deposited films. Less damages and uniformity of SnO_2 films are obtained by the condition of 15 mTorr and 50 W under the Co center magnet system. As a simple and practical method to obtain less damage films, a ring plate of masking glass method is proposed.

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