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# High-intensity oxygen cluster ion beam generation and its application to cluster ion-assisted deposition

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**Abstract.** Oxide film formation using high-intensity oxygen cluster ion beams has been developed. This deposition process uses large cluster ions, which can transport thousands of atoms per ion with very low energy per constituent atom. As a result, the interactions between the cluster and substrate atoms occur in the near-surface region, and cluster ions can deposit their energy with a high density in a very localized surface region. Enhancement of the oxidation reactions is clearly demonstrated. High-quality tin-doped indium-oxide (ITO) films, which are widely used in electrical and optical devices, are formed. Very smooth, highly transparent (> 80%) and low-resistivity ($< 4 \times 10^{-4}\,\Omega\,\mathrm{cm}$, which are the lowest values for films grown at room temperature) films, were obtained by the use of a 7 keV oxygen cluster ion beam. The energetic oxygen clusters collapsed at the surface and reacted with the metal atoms, and about 10% of them were incorporated when the kinetic energy of the cluster ion was above 5 keV. Oxidation reaction can be enhanced by energetic cluster ion bombardment, which offers a new technique for ion-assisted thin-film formation.

**PACS.** 36.40.-c Atomic and molecular clusters

## 1 Introduction

Clusters, which are aggregates of atoms or molecules, are interesting not only as a new state of matter but also as a new beam approach for material processing. It has been demonstrated that energetic cluster ion beams are very useful for surface processing, providing shallow implantation, high-rate sputtering, surface smoothing, cleaning, and film formation, as a consequence of the unique irradiation effects [1–13]. For example, when a cluster with the size of 1000 is accelerated with an energy of 10 keV, each constituent atom has only 10 eV, and these 1000 atoms collide with the surface within several $\mathrm{nm}^2$. Thus, clusters impact a surface with a low equivalent energy (low velocity) but with extremely high density.

There is a strong need to provide low-temperature oxidation processing for semiconductor and optical device fabrication. Energetic beams are quite useful for achieving low-temperature oxidation processing due to their excess kinetic energy [14–16]. We have demonstrated direct oxidation of silicon surfaces at room temperature with a low-energy oxygen cluster ion [3, 5] and also $PbO_2$ film formation under oxygen cluster ion irradiation during Pb evaporation [10].

Furthermore, high-quality tin-doped indium oxide (ITO) film formation at room temperature has been reported recently [13]. ITO has been applied to optoelectronic devices, such as transparent electrodes of flat panel display devices and photovoltaic devices, because of the low resistivity ($\sim 10^{-4}\,\Omega\,\mathrm{cm}$) and the high transparency to visible light (above 80% at 550 nm) [17–20]. However, better electrical and optical properties and surface morphology are required for various advanced optoelectronic device applications. Specifically, the transparent electrode used in color liquid crystal displays (LCD) needs to be formed on an organic color filter that is heat-sensitive. The temperature during film formation has to be kept below 150 °C. However, it is difficult to form high-quality films in this temperature range with the current techniques, e.g., magnetron sputtering or vacuum evaporation [17].

A lot of effort has been made toward the formation of low-resistivity ($< 1 \times 10^{-4}\,\Omega\,\mathrm{cm}$) ITO films. It was found that energy control of the incident species (atoms or molecules) is critical for reducing resistivity. When the energies of the incident species are high, resistivity of the film increases due to damage. When the energies are very low, enhancement of oxidation is suppressed. Therefore, the energy of the incident species ranges from a few to a few tens eV. The cluster ion beam has a suitable energy to meet this requirement. In this paper, oxygen cluster ion beams have been utilized in low-resistivity ITO film formation.

## 2 Cluster ion-assisted deposition system

A schematic diagram of the cluster ion-assisted deposition equipment is shown in Fig. 1. This equipment consists of three vacuum chambers, which are evacuated by different pumping systems. Two carbon crucibles, located in the deposition chamber, are heated by tungsten wire for evaporation of metallic indium and tin. The deposition rate of in-

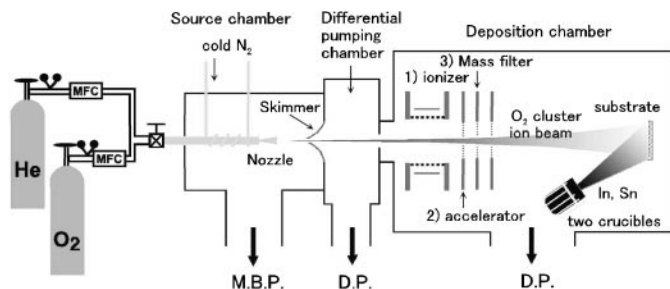


**Fig. 1.** Schematic diagram of gas cluster ion assisted deposition system.

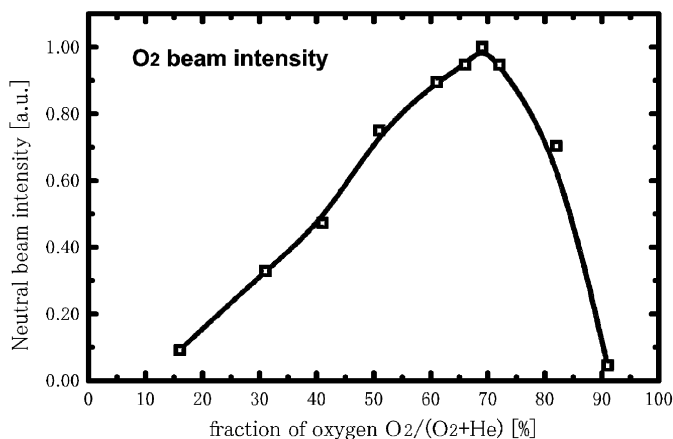


**Fig. 2.** Beam intensity of oxygen cluster as a function of fraction of oxygen.

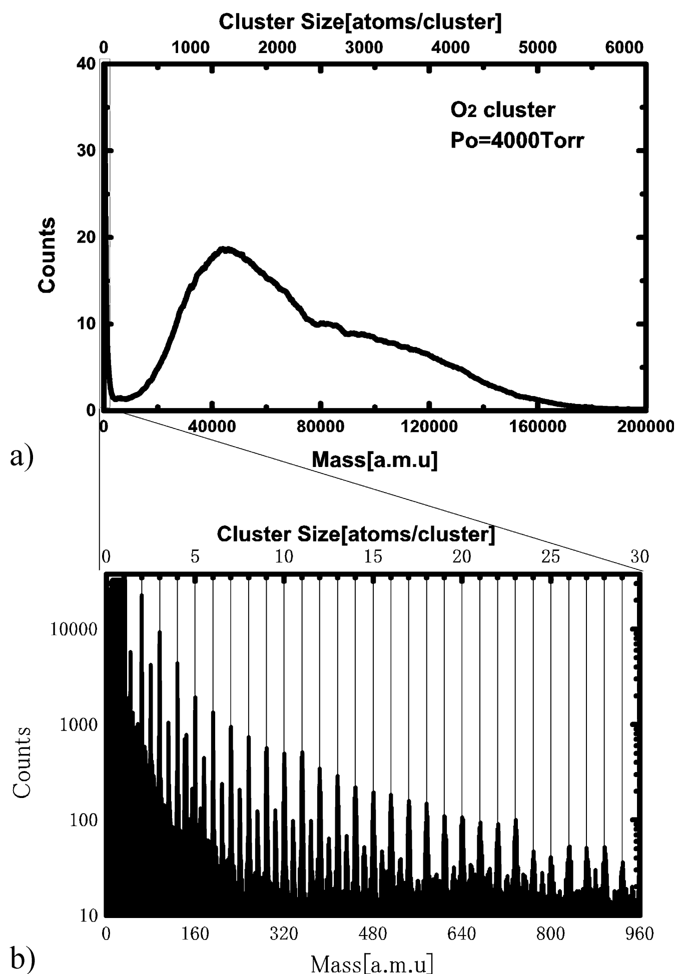


**Fig. 3.** Typical TOF spectra of oxygen cluster beam.

dium and tin can be controlled independently up to about 200 Å/min. by adjustment of the crucible temperature and can be monitored *in situ* during growth by a crystal thickness monitor.

The technique for the generation of gas cluster ion beams and for cluster-size separation has been described previously [4, 13]. Oxygen cluster beams were formed by adiabatic expansion through a Laval nozzle into the vacuum chamber. The clusters were ionized by electron bombardment, and the size selection of the cluster ions was performed using the retarding technique.

The cluster source was cooled down to 120 K, with $N_2$ gas refrigerated by liquid $N_2$, to increase the oxygen cluster beam intensity. As a result, the neutral beam intensity of $O_2$ clusters was increased by approximately 10 times its value at 300 K. Oxygen diluted with helium was utilized for source gas. As is shown in Fig. 2, the cluster beam intensity reached the maximum value at a 70% mixture ratio. Thus, high-intensity oxygen cluster beams were obtained by the dilution of $O_2$ gas with He gas and cooling of the inlet gases [3, 5].

Oxygen clusters were introduced through the skimmer and differential chamber into the deposition chamber. They were ionized by electron bombardment with an ionization voltage of 150 V and an electron current of 45 mA. High-current oxygen cluster ion beams of a few $\mu$A were obtained. The current density was about 300 nA/cm$^2$, which corresponded to about $4 \times 10^{15}$ molecules/cm$^2$/s. The intensity of the cluster ion beam provided in this system was sufficiently high to oxidize metallic indium during evaporation.

The cluster size distribution was measured using a time-of-flight (TOF) technique. Cluster beams were ionized by electron bombardment with an energy of 70 eV in the Wiley–MacLaren-type TOF system. The duration time of the extraction pulse was 10 $\mu$s, and the repetition rate was 200 Hz. Figure 3 shows typical TOF spectra of an oxygen cluster beam. Oxygen cluster size distribution ranges upto several thousand with a mean of about 2000. As shown in Fig. 3a, the mass resolution of the TOF system used in this study is too poor for observation of the peaks of each cluster size. However, each size of oxygen cluster can be resolved well, as is shown in Fig. 3b, when the cluster size is small ($N < 30$).

## 3 ITO film formation

The formation of indium oxide films on glass substrates at room temperature was examined with an oxygen cluster beam irradiation in conjunction with the evaporation

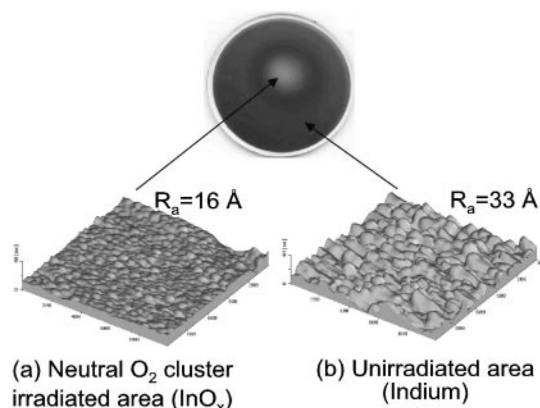


**Fig. 4.** Optical and AFM images of the films with oxygen cluster irradiation (a) and without irradiation (b).

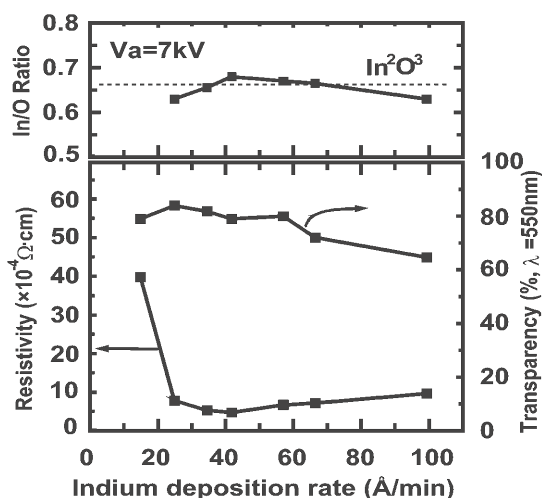


**Fig. 5.** Indium deposition rate dependence of resistivity, transparency and In/O ratio.

of metallic indium. The film with the thickness of 250 Å was grown at an indium deposition rate of 0.3 Å/s. Figure 4 shows the optical and atomic force microscope (AFM) images of the surface for the area with oxygen cluster irradiation (Fig. 4a) and without irradiation (Fig. 4b). The irradiated area becomes atomically smooth and visibly transparent as compared with the unirradiated area. According to observation with a scanning electron microscope (SEM), metallic indium was precipitated in the unirradiated area [13]. It is known to be quite difficult to obtain transparent films in oxygen ambient at room temperature, and thus the result indicates that an oxygen cluster without acceleration has higher chemical reactivity than oxygen molecules. However, the transmission efficiency and resistivity of the films deposited with an unaccelerated cluster beam is not sufficient for optical applications. Highly transparent ($> 80\%$) films were obtained when oxygen clusters were ionized and accelerated at an energy of above 5 keV [13]. Thus, the oxidation reaction is enhanced significantly by energetic oxygen cluster ion irradiation. When the mean cluster size is 2000, the average kinetic energy of the oxygen molecules in the cluster with the energy of 5 keV is only 2.5 eV. This energy is well below the threshold energy for damage formation. As a consequence, films with low resistivity were obtained.

Figure 5 shows the dependence of the In/O ratio, resistivity, and transparency on the indium evaporation rate. These samples were deposited at room temperature with various indium deposition rates, while the ion current density (300 nA/cm$^2$) and energy (7 keV) were kept constant. The lowest resistivity of $4 \times 10^{-4}\,\Omega$ cm with a transparency of 80% was obtained at an indium rate of 42 Å/min. This is the lowest value of resistivity of ITO films grown at room temperature to our knowledge. The In/O ratio decreases slightly with increasing deposition rate. Even though the indium deposition rate was as high as 100 Å/min., stoichiometric $In_2O_3$ films were obtained. The number of oxygen atoms contained in the cluster ions was about $4 \times 10^{15}$ molecules/cm$^2$/s. Therefore, approximately 10% of these oxygen atoms were incorporated into the films under these deposition conditions. It is thus evident that the bombardment effect of cluster ions offers a new ion-assisted thin-film formation technique.

## 4 Summary

High-intensity oxygen cluster ion beams were generated by supersonic expansion. The average size of the cluster ions was about 2000 according to TOF measurements. The current density of the cluster ion beams was about 300 nA/cm$^2$, which corresponded to about $4 \times 10^{15}$ molecules/cm$^2$/s. High-quality $In_2O_3$ films were obtained by $O_2$ cluster ion-assisted deposition at room temperature. About 10% of oxygen atoms in the cluster ions were incorporated into the films, when the kinetic energy was above 5 keV. Films with the lowest resistivity of $4 \times 10^{-4}\,\Omega$ cm, with a transmission greater than 80%, were deposited over a wide range of indium deposition rates of 30–100 Å/min. The bombardment effect of cluster ions offers a new ion-assisted thin-film formation technique.

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