Formation of Yttrium Oxide Clusters Using Pulsed Laser Vaporization

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Received November 19, 2004

Key Words : Yttrium oxide, Cluster, Laser vaporization, TOF mass spectrum

In recent years, the growth and characterization of Y_2O_3 films have been extensively investigated because of the numerous and important applications concerning electric and optical devices such as metal-insulator-semiconductor, transistor gates, dielectric layer in electroluminescent display, and host matrices for phosphor in cathodoluminescent displays.[1-4] The properties of Y_2O_3 film, large dielectric constant, high band gap energy, and energy transfer to activator in phosphor, *etc.* are related to defect formation in the crystal system.[5-7] The stoichiometry of oxygen atom and the oxidation state of metal atom significantly affect the formation of crystal defect in deposition of metal oxide thin film. Therefore, oxide films are normally cooled in high oxygen pressures to compensate for the incomplete oxygenation and improve the film properties.[8,9] However, in case of Y_2O_3:Eu system, it was reported that metal-rich Y_2O_3:Eu phosphor film has the higher luminescence efficiency than that of the stoichiometric Y_2O_3:Eu thin film post-annealed under oxygen atmosphere by Kumar *et al.*[10]

Pulsed laser vaporization of refractory solids such as yttrium oxide is increasingly employed in important applications, including thin film growth *via* redeposition of ablated materials as well as sampling for mass spectrometry.[11-13] Coupling of ionization laser with mass spectrometric techniques provides identification of molecular, fragment and cluster ion formation occurring in the ejected plume by ablation laser. While a broad range of experimental studies on molecular yttrium oxides have been investigated,[13-17] there are only a few studies dealing with small yttrium oxide clusters.[18] Although a number of studies have identified clusters directly formed by ablation into vacuum, typically a buffer gas is used to induce aggregation of small ablated species into clusters. The discovery of large clusters in the gas phase has stimulated broad interest in synthesizing clusters by laser ablation.[19-23] This work focuses on identifying the Y_2O_3 cluster during the laser ablation followed by supersonic expansion and pointing out the contribution of clusters in carrying oxygen from the target to the film in the pulsed laser deposition process.

The overall experimental system has been described in detail elsewhere.[24] The general outline of the experimental scheme will be presented in this report. The yttrium oxide clusters are produced by laser ablation of an yttrium oxide target into a helium carrier gas mixed with up to 5% of oxygen. The pulsed oxygen/helium flow from a solenoid valve (R.M. Jordan Co) operated at backing pressure 60 psi is injected through 0.8 mm-diam. nozzle in the laser ablation source. The yttrium oxide target is ablated at laser energies of 1-10 mJ/pulse by a laser beam (532 nm, SHG of Nd:YAG laser) directed perpendicularly to the carrier gas. The laser beam is focused by an f = 100 cm lens on the surface of a rotating and translating drum coated with yttrium oxide powder. About 3.25 cm downstream from the ablation spot, the clusters are entrained in the carrier gas flow freely expanded into vacuum, and are carried by the ensuing molecular beam through a 1.5 mm skimmer into the ion source of a Wiley McLaren type time-of-flight (TOF) mass spectrometer where they are ionized by an ArF (193 nm) excimer laser (Compex 102, Lamda Physik).

The cluster ions produced by laser ionization are extracted perpendicularly to the molecular beam and enter a 1.8 m-long flight tube in which they are separated in arrival time according to their mass. At the end of the flight tube, the ions are detected by Galileo microchannel plate detector. Signals were accumulated 100 times using a digital oscilloscope to reduce the statistical error. Time delays between valve opening, firing the ablation laser, and firing the ionization laser are controlled by two digital delay generator DG535 (Stanford Research System).

Generation of a representative mass spectrum in laser ablation TOF mass spectrometry is dependent on a number of factors, including laser pulse energy, the interaction between laser beam and the sample, and the stability of the ion structure. Figure 1 shows a typical TOF mass spectrum of $Y_nO_m^-$ clusters using a non-seeded pure helium carrier gas. The peaks can be grouped according to the number of yttrium atoms. The mass difference between adjacent peaks in each group corresponds to one oxygen atom. The mass spectrum is dominated by yttrium oxide cluster ions, $Y_nO_m^-$ in the size range of n = 1-13. The cluster ion peaks observed in each metal grouping may be gathered into two series depending on the yttrium/oxide ratio in the cluster ions. The cluster ion peaks can be described as consisting of the series of $Y_{2k}O_{3k-x}$ (x = 0, 1, 2, 3...) for the clusters of even number of yttrium or alternatively $Y_{2k-1}O_{3k-2-x}$ (x = 0, 1, 2, 3...) for those of odd number of yttrium. The number of oxygen in both of two series is deficient compared with stoichiometric ratio of the bulk phase Y_2O_3, and the formal oxidation states

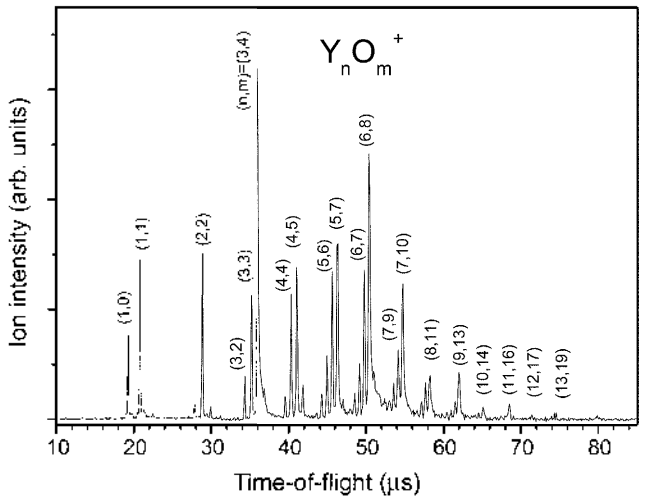

Figure 1. TOF spectrum of yttrium oxide cluster produced from laser vaporization source into an expanding supersonic jet of helium at 60 psi without oxygen. The numbers in parentheses, (n,m) above elected peaks denote the number of yttrium and oxygen atoms, respectively, in the cluster $Y_nO_m^+$.

of yttrium in the cluster ions can be represented in combination of Y^{+1}, Y^{+2} and Y^{+3}, assuming an oxidation state of –2 for the oxygen atom. The formation of clusters with the abnormal oxidation state of yttrium is consistent with the observation of metal-rich phase in XPS spectra of Eu-doped Y_2O_3 thin film deposited and cooled in vacuum under oxygen-free conditions.[10] The formation of oxygen-deficient yttrium oxide cluster ion in laser ablation is also consistent with the formation of metal-rich yttrium oxide cluster anion of the laser ablation of yttrium metal although the cluster anions could not be observed in this experimental system due to the positive acceleration field of TOF-MS.[18] The cluster ion peaks with x – 1 in each metal grouping are the most intense in both of two cluster series. They can be described as having series $(Y_2O_3)_{k-1}Y_2O_2^+$ for even numbers of yttrium and $(Y_2O_3)_kYO^+$ for odd numbers of yttrium, as noted in the earlier publication by Autriet *et al.*[25]

Figure 2 shows the series of mass spectra as a function of power of (a) ionization laser and (b) ablation laser in oxygen-free buffered gas. These spectra show the great stability of the intense series of cluster ions, $(Y_2O_3)_{k-1}Y_2O_2^+$, and $(Y_2O_3)_kYO^+$. As shown in Figure 2(a), at low power laser ionization, the TOF-mass spectrum is very congested due to non-stoichiometric cluster ion peaks (except most intense cluster ion series, $(Y_2O_3)_{k-1}Y_2O_2^+$ and $(Y_2O_3)_kYO^+$) in each yttrium grouping. As power of ionization laser increases at constant power of the ablation laser, the non-stoichiometric yttrium cluster ions decrease drastically whereas the distribution of cluster size is little affected. The ranges of the number of yttrium in cluster observed are n = 1-13 for ionization laser power of 3.2 mW and n – 1-12 for ionization laser power of 16.4 mW. This represents that the unstable non-stoichiometric neutral clusters formed in expansion of plume after ablation are fragmented into more stable cluster ions in ionization process by excess energy of

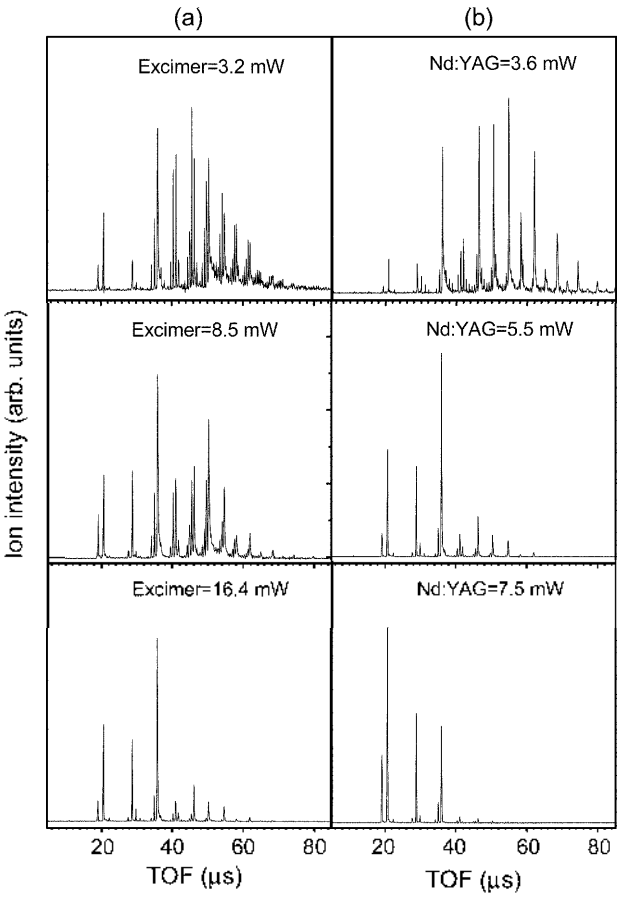

Figure 2. Laser power dependence of TOF spectra of yttrium oxide cluster produced from laser vaporization source under oxygen free condition; (a) TOF spectra according to variation of power of ionization laser at 5.5 mW of ablation laser power (b) TOF spectra according to variation of power of ablation laser at 16.4 mW of ionization laser power.

ionization laser. The ion signal (S) is related to the laser intensity (I) and the number of the absorbed photon (n).

$$S_1/S_2 = (I_1/I_2)^n$$

Though the ionization energy of yttrium oxide cluster has not been studied, it was reported that the ionization energy of YO is 6.11 eV.[26] Considering the photon energy, 6.42 eV of ArF excimer laser, ionization of yttrium oxide clusters can be suggested to be a single photon process. The fitted value of n for large stoichiometric clusters (k > 2) from ion signal dependency on ionization laser power is about 0.9, which is similar to 1 expected from photon energy and ionization energy of YO. However, for small stoichiometric clusters (k = 0, 1) this dependency is about 1.8 which is larger than that of the expected value. Though it is difficult to state an exact number of absorbed photons because saturation of further absorption beyond single photon absorption can occur, this larger power dependence also indicates that the non-stoichiometric clusters formed by ablation laser are easily fragmented into smaller cluster in ionization process. This shows that the non-stoichiometric cluster ions are much more unstable compared with the stoichiometric series of

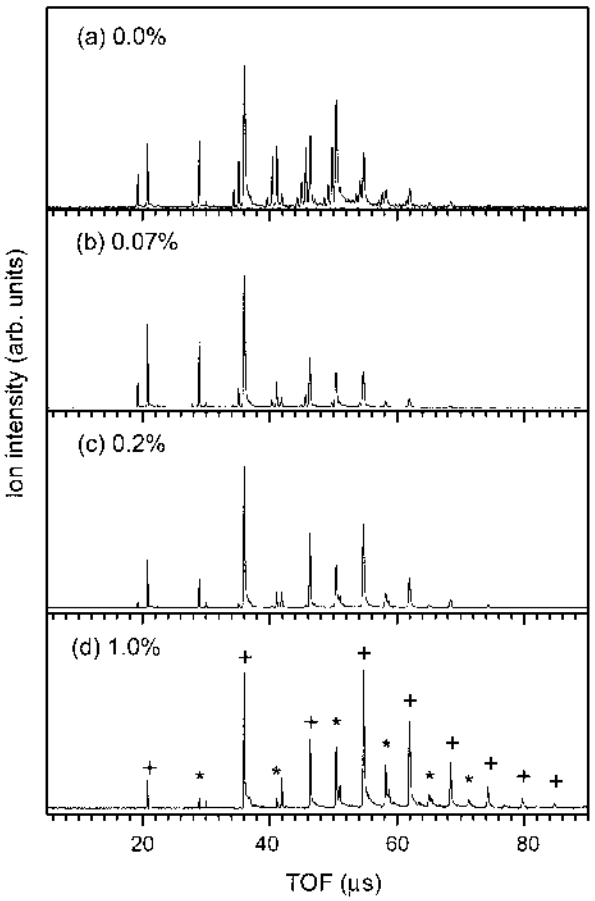

Figure 3. TOF spectra of yttrium oxide cluster according to variation of oxygen content; (a) 0%, (b) 0.07%, (c) 0.2%, and (d) 1.0% oxygen seeded in 60 psi He gas. The laser power is 5.5 mW for ablating laser and 8.5 mW for ionization laser, respectively. In spectrum (d), + and * denote the peak of $(Y_2O_3)_kYO^+$ and $(Y_2O_3)_{k-1}Y_2O_2^+$, respectively.

cluster ions.

Figure 2(b) shows the distribution change of cluster according to variation of ablation laser power. The size range of yttrium oxide clusters decreases rapidly from n = 1-19 to n = 1-7 as power of the ablation laser increases at constant power of the ionization laser. It is well known that collisions and cooling are required for cluster formation in supersonic expansion. In fact, pulsed molecular valve cluster sources utilize laser ablation of a material into an inert gas. The ablated materials with carrier gas are expanded through a nozzle jet to induce condensation. As the power of ablation laser increases, the plume ejected from yttrium oxide surface becomes highly energetic. The thermal energy of plume reduces the cooling efficiency of molecular beam and can prevent the growth to large clusters in the expansion zone of a supersonic jet.

Figure 3 shows a series of mass spectra as a function of oxygen content seeded in He carrier gas. The mass spectra exhibit two main characteristics. One is the distribution change of clusters. The intensity of oxygen-deficient yttrium oxide clusters decreases suddenly as oxygen content in seeded gas increases, and the size of stoichiometric yttrium oxide clusters produced increases. The largest size of yttrium cluster observed increases to m = 21 at 1.0% of oxygen content from m = 13 at the oxygen free condition, and the cluster peak with maximum intensity is shifted to larger yttrium oxide clusters with the vanishing of the Y and YO peaks. This observation may also reflect the growth of cluster from small entities (rather than by direct ejection) as suggested by K. K. Gibson in the postulated gas phase aggregation mechanism.[27] The other effect of oxygen content in the expansion gas shown in the spectra is the change of intensity ratio between the two intense cluster ion series. The relative total intensity ratio of $(Y_2O_3)_kYO^+$ composed of only trivalent yttrium to $(Y_2O_3)_{k-1}Y_2O_2^+$ containing divalent yttrium increases to about 3.0 at 1.0% of oxygen content from 1.33 under the oxygen free condition. This decrease of cluster series with divalent yttrium under high oxygen content can explain the formation of stoichiometric Y_2O_3:Eu film when it was post-annealed in high oxygen pressure. No further oxidation takes place to form the higher valence oxidation state of yttrium at increased oxygen partial pressure. This result suggests that trivalent yttrium species are stable in the gas phase.

In conclusion, nonstoichiometric yttrium oxide clusters are generated by ablation of an yttrium oxide target under oxygen free conditions. The distribution of yttrium oxide clusters and the formal oxidation state of yttrium atom are much affected by laser power and oxygen content of the seeded gas. These data can be employed to help explain the luminescence properties and structure of Y_2O_3:Eu thin film deposited by a pulsed laser deposition.

Acknowledgment. This work was supported by Soongsil University.

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