Plasma-assisted Evaporation of Titanium Dioxide Films

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Abstract

Titanium dioxide films were formed by means of plasma-assisted evaporation technique. Ti was used as evaporation source and heated by electron beam. The necessity of creation plasma during evaporation were discussed together with the film quality and the geometrical setup of the system. Creation of plasma during evaporation of Ti played a very important role in order to form TiO_2 films with good quality and the Ti cluster size also affected to the refractive index of the deposit.

Introduction

Plasma-assisted evaporation technique is an interesting technique because the deposition rate is higher and the substrate temperature is lower than that of sputtering technique. Moreover, this is able to solve the problem of the damage of the substrate by charged particles from plasma in sputtering, which limits the deposition rate of sputtering [1]. Therefore, this technique can be applied to thin film formation on plastic substrates. However, the film properties, such as electrical conductivity, refractive index, and so on, are slightly poor, because of the difference in particle size. A number of papers on the formation of titanium dioxide (TiO_2) by means of PVD methods. TiO_2 films are chemically resistive and have a high refractive index in the visible and the infrared region [2]. These properties make TiO_2 an attractive material for use as optical thin films. The objective of this study is to deposit thin films of stoichiometric

TiO_2 by plasma-assisted evaporation technique using Ti as evaporation source in order to increase deposition rate. The properties of TiO_2 obtained by this method should be comparable to films deposited by sputtering, using Ti and TiO_2 targets. Furthermore, the role of plasma in the formation of TiO_2 films is discussed together with the consideration of the shape of evaporant cloud.

Experimental

Experimental apparatus is shown in Fig. 1. A batch type system with electron beam gun, of which maximum power is 10 kW, was used. The evaporation source consisted of 99.8 % pure Ti metal. The distance between the source and the substrate was changed within 400-700 mm and the spot size of the electron beam was 175 mm^2. Oxygen inlet position was changed and oxygen gas was introduced into the system so as to oxidize the evaporant. Typically the oxygen partial pressure was kept in the range of $5x10^{-2}$ Pa to $7x10^{-2}$ Pa. An rf coil electrode was placed between the source and the substrate. The compound deposited onto a glass or polyester substrate and its quality was evaluated. Optical emission spectroscopy (OES) and probe measurement were carried out as plasma diagnostics.

Results and Discussion

Electron temperature (T_e) and electron density (n_e) were measured about pure oxygen plasma in the absence of evaporant in order to obtain the information on plasma. The result is shown in Fig. 2. In this case, the measurement was carried out using triple probe technique and the probe was inserted to the chamber from two different directions. When the plasma was created at 500 W and $6x10^{-2}$ Pa, T_e was about 4 eV and n_e was about $4x10^9$ cm^{-3} at position *A*, respectively. Although T_e decreased with increasing distance between the coil and the substrate, n_e did not change. Both T_e and n_e were influenced by power input and pressure. In pure oxygen plasma without evaporant, spectra due to $O_2(B^3\Sigma_u^- - X^3\Sigma_g^-)$, $O_2^+(b^4\Sigma_g^- - a^4\Pi_u)$, and O atomic lines were identified. When Ti was evaporated without creating oxygen plasma, Ti atomic lines were identified near the evaporation source. By introducing oxygen into the system, spectra due to Ti and $TiO(A^3\Phi - X^3\Delta,\ C^3\Delta - X^3\Delta)$ in addition to weak spectra due to O_2, O_2^+, and O were identified only near the source. Moreover, such species were also existed upper position of the coil when plasma was created and the intensities of the spectra due to O_2, O_2^+, and O were strengthen. The intensities due to these species were also affected not only by power input and pressure but also by electron beam power. Thus, the deposition of TiO_2 films were carried out using such plasma as assistance.

In order to consider the plasma-assisted evaporation, the distribution of the vapor cloud during deposition was determined by experiments and mathematical approximation. As shown in Fig. 3 the actual shape of the evaporation cloud in the evaporator, only the top portion can be approximated by Knudsen's cosine law because of the shape of the crucible. Owing to the positioning of the coil and the increased collision frequency the shape no longer follows a cosine distribution. Outside the rf coil the deposit will have a different properties. From the plot of varying thickness with changing position of the substrate, it is seen that the maximum thickness of the deposit is 0.1 m away from the evaporation source, within the coil. From these results, substrate placed in the region where the plasma concentration was high and which was well inside the Ti vapor cloud had the best film quality.

The deposits onto the glass substrate, which was formed by a certain condition, were identified by XPS, XRD and ellipsometry (λ =632.8 nm). The results are summarized in Table 1 comparing with those obtained by sputtering technique. Films obtained in oxygen flowing without creating plasma were amorphous. Although crystallity of the film obtained without creating plasma could be improved by post-annealing in a vacuum more than 400 K, the films obtained were identified to be several kinds of suboxides. However, anatase-type TiO_2 was obtained when oxygen plasma was created. All deposits showed interference colors as given in Table 1. The binding energies of the surface of the deposits when the plasma was created corresponded to those of Ti-O bond in TiO_2. The refractive indices of the deposits without plasma creation was less than 2.0 and that with plasma was more than 2.1. These values were smaller than that obtained by sputtering.

As shown in Fig. 4, rf power seemed to have some effect on improving the refractive index of the deposits. In this case, the acceleration voltage of electron beam was maintained at 6 kV. It is not absolutely clear why the refractive index improves when a high power plasma is used. The original hypothesis, that the plasma improves reactivity of oxygen with Ti, is not convincing as the films does not show any visible difference in color. It is more likely that the crystalline structure of the film may be the dominant factor in altering the refractive index. The formation of anatase-type films is only possible at a substrate temperature above 400 K [2]. Films deposited below this critical temperature have a amorphous structure, and therefore a low refractive index. Subsequently, a deposited TiO_2 thin films which originally had a low refractive index, was heated in a vacuum at 400 K for 1 h. Originally film had a refractive index of 1.86 but after the heat treatment it improved to 2.4. This leads to the conclusion that in case of TiO_2 deposition the post important effect of the plasma is that it increases the substrate temperature. However, heating the deposited films is not desirable as it requires very strict control, in order to prevent the loss of oxygen from the thin film. Therefore, further experiment was required to deposit anatase-type TiO_2 films without any further treatment. It is thought that one of the reasons for films quality is the size of the deposited particle, that is the size of Ti cluster because it would be difficult to oxidize Ti sufficiently. For reducing the cluster size, Ar-oxygen or nitrogen-oxygen plasma was used as assistance. The results are given in Table 2. Addition of Ar resulted in deposition of film that was colorless and lower refractive index. This was because of amorphous nature of the films. However, addition of nitrogen improved the refractive index to about 2.3. In presence of a plasma, oxygen and nitrogen turn to NO, which is an oxidizing agent. Increase of refractive index could be because o this effect. Moreover, acceleration voltage of electron beam is also one of the important factor to reduce cluster size. When the deposition was carried out at the same condition except the voltage, the refractive indices were 2.2 for 6 kV and 2.4 for 4 kV, respectively.

Thus, it is found out that the creation of plasma during evaporation of Ti played a very important role in order to form TiO_2 films with high quality and the cluster size also affect to the good film formation.

Conclusion

(1) Creation of plasma was necessary for the deposition of stoichiometric TiO_2 films by reactive evaporation.

(2) Without the use of the plasma, the refractive index for films deposited by plasma-assisted evaporation was 1.9; with the plasma the refractive index was increased to 2.4 when conditions were optimum.

Acknowledgment

We would like to thank Mr. K. Kiyokawa for his plasma diagnostics measurement.

References

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Table 1 Comparison of deposits

Method	Source	P_{rf} (W)	P_{EB} (kW)	P_{O_2} (Pa)	n	Rate (nm/s)	Ts (K)
Evaporation	Ti	0	1.2	6×10^{-2}	1.86	1.5	350
	Ti	500	1.2	6×10^{-2}	2.25	1.2	400
	Ti_3O_5	500	1.2	6×10^{-2}	2.10	0.8	400
Sputtering	Ti	300	0.1		2.20	0.02	450
	TiO_2	200	0.1		2.35	0.02	450

Sputtering:5 sccm O_2/50 sccm Ar

Table 2 Effect of plasma assistance

Plasma	P_{rf} (W)	P (Pa)	n	Remarks
$Ar-O_2$	500	6×10^{-2}	1.78	Colorless
N_2-O_2	500	6×10^{-2}	2.30	Green film turns to red
O_2	500	6×10^{-2}	2.25	Greem film turns to red

EB:6 kV-300 mA, 10 sccm Ar, O_2/100 sccm O_2

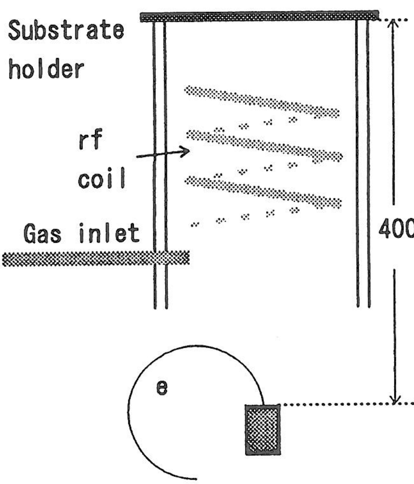

Fig. 1 Experimental setup

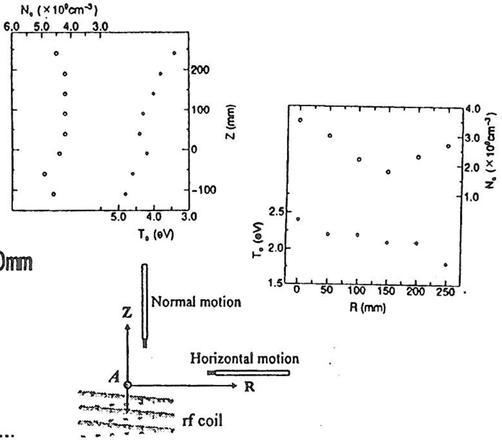

Fig. 2 T_e and n_e of O_2 plasma

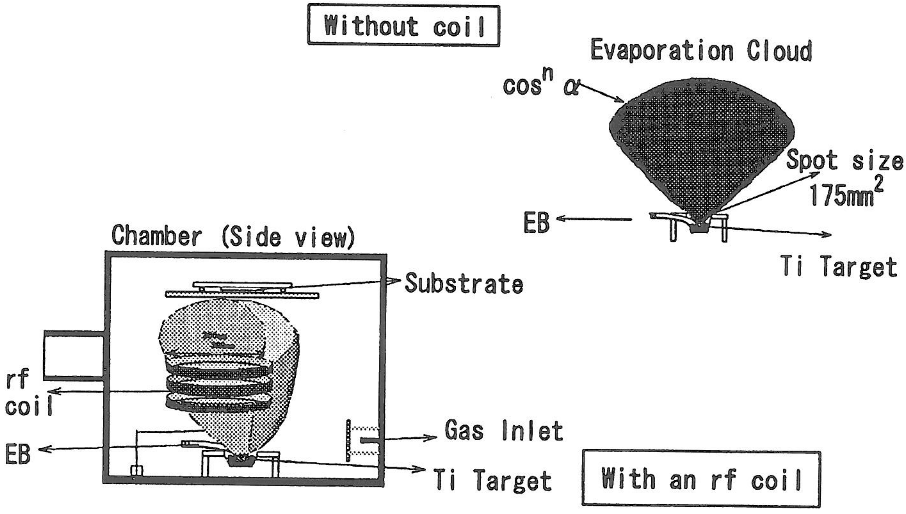

Fig. 3 Actual shape of the evaporation cloud

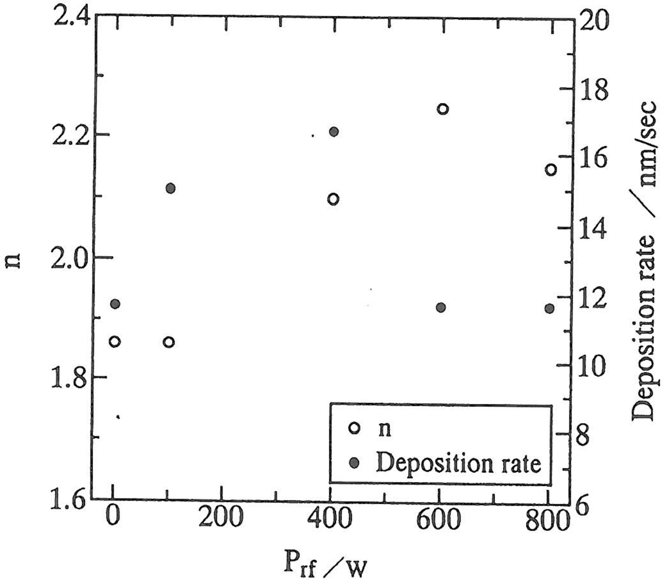

Fig. 4 Effect of rf power