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Characterization of SiO_2 Films by Photo-CVD using a Xe_2 Excimer Lamp

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Recently, much attention has been paid to novel photochemical vapor deposition using vacuum ultraviolet (VUV) excimer lamps (VUV-CVD), because thin films can be deposited at room temperature. We show some characterization of SiO_2 films and discuss about the reaction mechanism using organic siloxane precursors as chemical precursors.

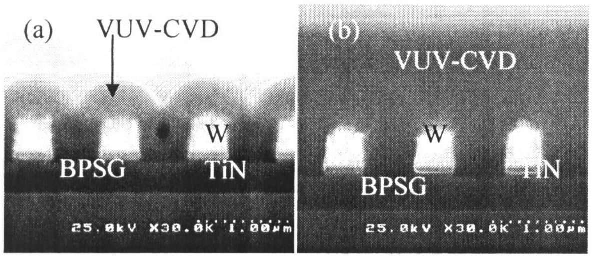

Fig.1. Cross sectional views of films deposited on line-and-space structures from TEOS (a) and TEOS+O_2 (b).

Fig.1 shows cross sectional views of films deposited on line-and-space structures of W/TiN. The film in (a) deposited from tetraethoxyorthosilicate (TEOS : $Si(OC_2H_5)_4$) only shows no conformal step coverage property included voids between lines. This finding implies that the reactants are adsorbed on the substrate surface and react without significant surface migration. The reaction mainly occurs in the gas phase. In case of adding O_2 to TEOS, both activated oxygen and ozone generated by the VUV photons efficiently dissociate TEOS molecules. The film in (b) shows the same self-flatness step coverage property as conventional O_3-assisted AP-CVD in which macromolecules formed by TEOS and O_3 are adsorbed and migrate on the surface. The main reaction occurs on the surface. Then adding O_2 changes VUV-CVD reactions from the gas phase to the surface.

Fig.2 shows FT-IR spectra taken from TEOS vapor (a), VUV-CVD films deposited using TEOS only (b) and adding O_2 to TEOS (c). TEOS vapor consists of main peaks of Si-O-CH_2-CH_3 at 1095cm^{-1}, Si-O-Si at 1075cm^{-1} and –CH_2-CH_3 around 2960cm^{-1}. The spectrum (b) consists of not only a main peak of Si-O-Si at 1075 cm^{-1} but also small peaks of Si-O-CH_2-CH_3 and –CH_2-CH_3. TEOS molecules are not completely dissociated by VUV photons, and then radicals that are Si-O of main structure of TEOS and CH impurities are adsorbed on the surface and result in a film included C and H. By adding O_2 to TEOS, the amount of C-H impurities decreases but O-H impurities are incorporated whose absorption peaks appear around 3600 ~ 2800cm^{-1}. In this case, ozone and activated oxygen generated by VUV photons dissociate C-H and generate O-H. Then O_2 gives the strong effects films structures. The VUV-CVD films using TEOS consist of SiO_2 and impurities caused by an organic precursor.

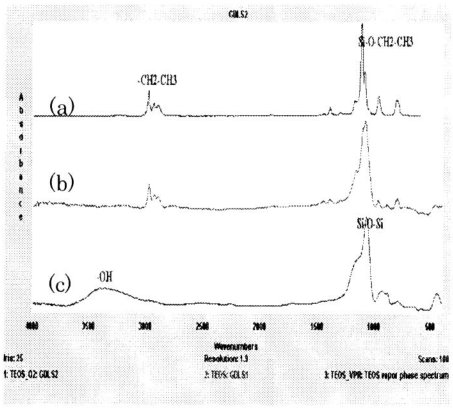

Fig.2. FT-IR spectra by TEOS (a) TEOS vapor, (b) film from TEOS and (c)film from TEOS+O2.

VUV photons dissociate organic precursors into radical reactants of Si-O and impurities such as C-H and O-H. The reactants finally condense on the surface into deposition films included SiO_2 and impurities. The reaction is different by adding O_2. It is caused by the behaviors of ozone and activated oxygen that VUV photons dissociate O_2 and are generated. The film deposition at room temperature in VUV-CVD that either thermal or plasma induced damages are completely avoided must become a novel technique in thin films preparations.

Table I. Characteristics of films deposited from various kinds of precursors.

Precursor	Addition gas	Growth rate (A/min)	Gap filling
TMOS	None	35	Conformal
	O_2	87	—
HMDSO	None	212	Flow
	O_2	751	Deposition in the grooves
TOMCATS	None	137	Conformal
	O_2	1085	Much deposition on tops
DMDMOS	None	86	Flow
	O_2	95	Self-flat
FTES	None	10	—
	O_2	68	—
PTES	None	75	—
	O	—	—

Films are deposited by using TMOS ($Si(OCH_3)_4$), HMDSO ($(CH_3)_3SiOSi(CH_3)_3$), TOMCATS ($(SiOHCH_3)_4$), DMDMOS ($Si(OCH_3)_2(CH_3O)_2$), FTES ($Si(OC_2H_5)_3F$) and PTES ($C_6H_5(C_2H_5O)_3Si$). The characteristics of the films are summarized in Table I. The maximum growth rate more than 100 nm/min is obtained by using TOMCATS+O_2. The structures are very different from one film to another. We are very interested in the film deposition mechanisms for each precursor, but it is in future problem.

In conclusion, we have clearly shown the VUV photons dissociate effectively various kinds of precursor molecules to result in the SiO_2 film deposition at room temperature. The maximum deposition rate more than 100 nm/min was obtained from TOMCATS+O_2. The growth mechanisms and characteristics of the films largely depend on the precursors, which means that the VUV-CVD opens various application fields for film growth.