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Studies of the main factors on the structural formation of TiO_2 thin films by pulsed laser deposition

Ha-Sub Yoon, Seong Kyu Kim, *Sang-Hyeob Kim, and *Hoong-Sun Im

Department of chemistry, Sung Kyun Kwan University
**Surface Analysis Group, Korea Research Institute of Standards and Science*

Since titanium dioxide(TiO_2) shows various attractive properties, such as high refraction index (n=2.5), high permittivity (>100), high dielectric constant, titanium dioxide thin films have been studied extensively by many researchers. Crystalline TiO_2 can exist in three phases: brookite, anatase, and rutile. Rutile is known to be the most stable phase, while other are thermodynamically less stable. Due to its scientific and practical importance, TiO_2 rutile has been the subject of many experimental and theorectical investigations. Recently, the anatase also has been received the attention because of its different electronic properties from the rutile. Even though the films can been prepared by various techniques such as chemical vapor deposition(CVD), electron beam assisted evaporation, RF magnetron sputtering, and pulsed laser deposition technique(PLD), the deposition parameters should be properly controlled to obtain the film of single phase anatase or rutile phase.

We have deposited TiO_2 thin films by PLD on single crystal of Si substrate(100) using Nd:YAG laser. The PLD technique is easy to set up and by optimizing the experimental conditions, films with the same stoichiometry as the target can be obtained. The structure of TiO_2 film was found to be very dependent on the deposition parameters. From the experimental results, the main factors on the phase determination are discussed.

The experiments were carried out using a Q-switched Nd:YAG laser(a wavelength of 532 nm, a pulsed duration of 10 ns, a repetition rate of 10 Hz). We have studied that the films deposited on different substrate temperatures ranged from room temperature to 900℃, oxygen ambient pressures (P_{oxy}) of 0.01 torr to 1 torr, and laser fluences ranged from 0.5 J/cm^2 to 10 J/cm^2. The prepared films have been characterized by Scanning Electron Microscopy(SEM), X-ray Diffraction(XRD).

We found that the anatase as well as the rutile phases may form the original rutile phase of the target TiO_2. At P_{oxy} of 0.75 torr and the laser fluence of 0.5 J/cm^2, the film structures were mainly dependent on the temperature. That is, amorphous phase was formed below 300℃, only anatase phase was formed between 300℃ and 600℃, and above 900℃ only rutile phase phase was formed. Between 600 ℃ and 900℃, the mixture of anatase and rutile phases was obtained. At the lower P_{oxy} of 0.01 torr, however, only the rutile phase was obtained above 400℃.

With the same energy of the nucleation sites (the same substrate temperature), the rutile phase can be formed easily at the lower P_{oxy}. The kinetic energy of ablated particles is relatively high at the lower P_{oxy}. The higher kinetic energy helps

for ablated particles to overcome the activation energy for the formation of the rutile phase, which is found to be higher than that of the anatase phase. This kinetic energy dependence is also supported by the experimental results of the laser fluence studies. As laser fluence increased, the rutile peaks was getting more intense in the XPS spectrum that the anatase ones. When the energy of the nucleation sites is high (the higher substrate temperature), the lower kinetic energy is sufficient to allow rutile phase. In this case, the energy of the nucleation sites is high enough for the particles in the lower kinetic energy to overcome the activation energy for the formation of the rutile phase.

In conclusion, TiO_2 thin film in the form of the single phase can be deposited successfully by PLD using Nd:YAG laser. The phase formation of TiO_2 thin film is largely dependent on the function of the energy of the nucleation sites and the kinetic energy of the ejected particles. The anatase phase can be only obtained in the condition of the lower energy of the nucleation sites with the lower kinetic energy of the ejected particles, while the rutile phase can be formed with the higher energy of the nucleation sites and/or the higher kinetic energy of the ejected particles.