PREPARATION OF Nb BASED THIN FILM USING PULSED LASER DEPOSITION AND ITS ELECTRICAL PROPERTY

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ABSTRACT
PREPARATION OF Nb BASED THIN FILM USING PULSED LASER DEPOSITION AND ITS ELECTRICAL PROPERTY. The research for largering capacity of dielectric multi layer type capacitor using Pulsed Laser Deposition (PLD) method was carried out. In this study, we focus on the inexpensive material Nb as a substitute for expensive material Ta, which is currently used for ferroelectric material. The Nb-based (Nb₂O₅) and TiO₂ particle were deposited on Si/SiO₂ substrate at temperature of 600°C under the oxygen pressure of 5Pa, and Pt was used as the last layer. Doping of TiO₂ to the Nb₂O₅ was carried out by alternately replacing each target and finally the deposited film with a thickness of 200 nm was achieved. The capacity value of pure Nb₂O₅ thin film was higher than pure TiO₂, but TiO₂ was more stable against the changes of temperature. The capacitor that has a ratio of 30% Nb₂O₅ showed the highest capacity value. Single layer of Nb₂O₅ thin film has the largest rate of change in capacitance, and the capacitor that already doped by TiO₂ has a more less changes in capacitance against the changes of temperature. In order to crystallize, the capacitor was then annealed in the air for 12 hours at the temperature of 700°C. Same as before annealing, a mixed thin film thas has a ratio 30% of Nb₂O₅ still showed the highest capacity value, even there is a small changes against the changes of temperature. Other mixed thin film with different ratio of TiO₂ have more stable temperature characteristics, but the capacity value was very small. From above results, it can be considered that the thin film of 30% of Nb₂O₅ and 70% of TiO₂ is the best potential with highest capacity value and small changes against the changes of temperature.

Keywords: Nb Thin Film, Capacitor, Thin Film Fabrication, Electrical Property, Capacitance, Annealing

INTRODUCTION
Growth of electrical and electronic equipment industries are phenomenal in recent years. High-performance, miniaturization has been creating a new value. The advanced electronic devices, such as...
personal computer, mobile phones, and others are spreading rapidly. The forming of electrical and electronic industries, personalization have progressed, also the number of devices have been steadily increasing. Especially in the beginning of this century, the era of advanced information and telecommunications is predicted, a variety of information and communication network equipment is about to be developed.

It will be appreciated that, with respect to the electronic component has been strongly desired a small, high-performance, and low cost under such circumstances. Especially in the mobile phone that is booming now, the technological innovation is remarkable, the miniaturization and multi-functionality of mobile phone is one of the example [1].

It is expected that in the field of capacitor applications, faster CPU, reduction in size and weight of the equipment, digitization and advanced features make further progress. Among them, the size corresponding to such needs, thin size with large-capacity, low-impedance or high-frequency region, the development of multilayer ceramic capacitors such as reliability in terms of heat resistance is actively done. The past 10 years has been promoted ambitious large-capacity thinner dielectric layer, with multi-layered, among others.

In this research, the aimed is to produce thin film insulator by laser ablation, and to evaluate the characteristic of the thin film. The price of tantalum that is commonly used as a dielectric are soaring, and the research about substitute material is urgently needed. The study of Nb as the next generation material is studied. Nb is the most promising candidate because the price is cheaper, the deposit amount in the earth is 100 times [2-3], the density is a half, the dielectric constant is 1.5 times [4-9] than tantalum. Among them, NbO, NbO$_2$, and Nb$_2$O$_5$ are well known examples that show metallic, semiconducting, and electrical phases, respectively.

Particularly, Nb$_2$O$_5$ is a very versatile material having a large relative dielectric constant, and has been actively studied for various application. As film deposition technology has made rapid progress, niobium oxide films with different material properties have been produced for different purposes by using various growth methods: sputtering, plasma oxidation, molecular beam epitaxy, etc. [10-11]. From all of these methods, PLD is the easier one and have been attracted many scientist in recently. After depositing the high dielectric of niobium oxide that is used as a target on the Si (100) substrate, then the relationship between the composition ratio, crystal structure and dielectric constant were examined. In addition, the capacitor has been required to exhibit stable performance under a variety of usage, therefore, it is needed to produce the corresponding product. In this study, we were added TiO$_2$ at various ratio in order to improve the temperature characteristics.

**EXPERIMENTAL METHOD**

As a target of deposition, the sintered material of TiO$_2$ and Nb$_2$O$_5$ that is prepared in a pellet form, at the diameter size of 0.5 cm and thickness of 3.0 cm was used. The deposition of film was done on the Si (100) substrate. Figure 1 shows the Pulsed Laser Deposition (PLD) apparatus used for the thin film deposition. The apparatus is consist of chamber, vacuum pumping equipment and excimer laser oscillation apparatus. The vacuum exhaust system of chamber is composed from turbo pump and rotary pump, the vacuum degree was set in a high vacuum up to $1 \times 10^{-5}$ Pa. The laser used for deposition is a KrF excimer laser with a specification i.e. wavelength of 248 nm, pulse width of 22 ns, output shape of 32 mm × 10 mm, pulse maximum energy of 450 mJ, maximum average output of 70 W and pulse repetition rate up to the 200 Hz. Regarding with the process of thin film fabrication, firstly a laser beam emitted from the excimer laser oscillating apparatus was introduced into the vacuum chamber through mask attenuator, hole of mask with shape of 10 mm × 10 mm, quartz flat mirror and the entrance window made of quartz. Then, the laser was incident on the target with the irradiation angle of 45° against the target. The generated particles ablation were then deposited on the substrate.

After performing ultrasonic cleaning in acetone, the substrate and target were placed in the holder as shown in Figure 2. Four pieces of targets are possible to be installed during deposition. The target exchange can be done by revolving target holder. Furthermore, during the laser irradiation, the target is allowed to spin in order

![Figure 1. Schematic of Pulsed Laser Deposition apparatus](image1)

![Figure 2. Schematic of target changer and mask](image2)
RESULTS AND DISCUSSION

Figure 3 shows the phase composition of TiO$_2$ single layer thin film with the thickness of about 400 nm, which has been deposited using TiO$_2$ under 34783 shots of laser. The various composition of Titanium-Oxygen phases, such as TiO, TiO$_2$, and Ti$_2$O$_3$ were observed. The peak of Pt as an electrode part was also identified.

The composition of the mixed thin film (Nb$_2$O$_5$)$_x$(TiO$_2$)$_{1-x}$ were deposited by irradiating the laser alternately to the TiO$_2$ target and Nb$_2$O$_5$ target. The number of shots was adjusted to avoid the generation of single layer. By mixing alternately using deposition method, the mixed thin films were produced in atomic units. In order to irradiate two targets alternately by using excimer laser, it is needed to irradiate at the same cycle shot for each irradiation. Therefore, the number of laser shot for each target was adjusted and controlled. After the thickness of deposited thin film was 200 nm, the percentage ratio mixing of Nb$_2$O$_5$ inside the film can be calculated by multiply 100 to (thickness of Nb$_2$O$_5$/200 nm). Table 2 shows each parameter when produce a mixed thin film.

The composition of the mixed thin film was not uniformly crystallized. Thus, the crystallization was carried out by annealing inside the furnace that is heated to 700 °C. Then the change in dielectric constant in each composition was examined. The dielectric constant of the sample thin film was measured using Inductance, Capacitance, Resistance (LCR) meter by changing the frequency from 100 Hz to 1 MHz.
approximately 400 nm was observed. From this observation result, it showed that deposition control is possible to be carried out. The easiest way to control the deposition is to set the number of laser shots, as we have done in this research.

The capacitance value of Nb$_2$O$_5$ and TiO$_2$ single thin film is shown in Figure 6. At low frequency, Nb$_2$O$_5$ single layer capacitor has a better capacity comparing than TiO$_2$. The capacitance value decreases as the frequency is becoming higher. In the case of Nb$_2$O$_5$ single layer capacitor, the reduction of capacitance value against the increasing of frequency was greater than TiO$_2$.

Figure 7 shows the phase composition of mixed thin film, which ratio of Nb$_2$O$_5$:TiO$_2$ is 50:50. At the first XRD characterization, the peak did not appear, then it was decided to anneal for 12 hours to make crystallization. After annealing, the peak of rutile type TiO$_2$ was confirmed inside the thin film using XRD method. The peak of Nb$_2$O$_5$ and Pt were also identified. Comparing with the result in Figure 3 and 4, after doping Nb$_2$O$_5$ to TiO$_2$ and annealing process, the film that only contain TiO$_2$, Nb$_2$O$_5$, which was the original of target, and its mixing was obtained. This is also to proof that the process of producing mixed thin film by doping Nb$_2$O$_5$ here can eliminate the generation of other composition, such as TiO, NbO and others.

The capacitance value of deposited (Nb$_2$O$_5$)$_x$(TiO$_2$)$_{1-x}$ thin film that has fabricated by mixing Nb$_2$O$_5$ and TiO$_2$ at various ratio without annealing is shown in Figure 8. The figure shows the change of capacitance value at each frequency when changing the ratio of Nb$_2$O$_5$ inside the thin film from 10% until 90%. When the deposition of Nb$_2$O$_5$ particles achieved 30%, the thin films showed the highest capacitance value. However, in the high frequency range, the sample at any ratio showed a low value of capacitance.

Figure 9 showed the capacitance value in the case of high frequency between 500 kHz until 1 MHz. The
value of capacitance at ratio of 30% Nb$_2$O$_5$ showed the biggest value than the others. On the other hand, the value of capacitance of mixed thin film with 10% ratio of Nb$_2$O$_5$ was smallest, approximately more than 1/10 times in the case of 30% of Nb$_2$O$_5$.

CONCLUSION

The following conclusions have been obtained after summarizing the results. The reduction of capacitance value against the increasing of frequency in the case of TiO$_2$ was greater than Nb$_2$O$_5$. The mixed Nb$_2$O$_5$-TiO$_2$ thin films with the ratio 30% of Nb$_2$O$_5$ showed the highest capacitance value. The changes of capacitance against the changes of frequency was became smaller comparing with the case of pure TiO$_2$ thin film. Therefore, doping of Nb$_2$O$_5$ to TiO$_2$ is able to stabilize the capacitance changes with the increasing of frequency. It means Nb$_2$O$_5$ is potential to substitute the Tantalum for their using as electrode. However, the generation of other compound of Nb$_2$O$_5$ have to be surely controlled and be eliminated in the thin film production.

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