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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 (Nb_2O_5) and TiO_2 particle were deposited on Si/SiO_2 substrate at temperature of 600 ^oC under the oxygen pressure of 5Pa, and Pt was used as the last layer. Doping of TiO_2 to the Nb_2O_5 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 Nb_2O_5 thin film was higher than pure TiO_2, but TiO_2 was more stable against the changes of temperature. The capacitor that has a ratio of 30% Nb_2O_5 showed the highest capacity value. Single layer of Nb_2O_5 thin film has the largest rate of change in capacitance, and the capacitor that already doped by TiO_2 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 700oC. Same as before annealing, a mixed thin film thas has a ratio 30% of Nb_2O_5 still showed the highest capacity value, even there is a small changes against the against the changes of temperature. Other mixed thin film with different ratio of TiO_2 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 Nb_2O_5 and 70% of TiO_2 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

ABSTRAK

PREPARASI LAPISAN TIPIS BERBASIS Nb DENGAN METODE *PULSED LASER DEPOSITION* DAN SIFAT LISTRIKNYA. Telah dilakukan penelitian peningkatan kapasitas dari kapasitor tipe *multi layer* dielektrik memakai metode *Pulsed Laser Deposition* **(***PLD*) . Pada penelitian ini, difokuskan pada bahan Nb sebagai pengganti bahan Tantalum, yang saat ini dipakai sebagai bahan feroelektrik. Partikel berbasis Nb (Nb_2O_5) dan TiO_2 dideposisikan di substrat Si/SiO_2 pada suhu 600 ^oC dibawah tekanan oksigen 5 Pa, dan ditutup dengan Pt sebagai lapisan terakhir. *Doping* TiO_2 ke dalam Nb_2O_5 dilakukan dengan mengganti target deposisi, dan pada akhirnya diperoleh lapisan tipis dengan ketebalan sekitar 200 nm. Nilai kapasitansi lapisan tipis murni Nb_2O_5 adalah lebih tinggi dibandingkan lapisan tipis TiO_2, namun TiO_2 lebih stabil terhadap perubahan suhu. Kapasitor yang memiliki rasio 30% Nb_2O_5 menunjukkan nilai kapasitas tertinggi. Lapisan tipis murni Nb_2O_5 memiliki rasio perubahan nilai kapasitansi terbesar, dan kapasitor yang telah di*doping* TiO_2 memiliki sedikit perubahan nilai kapasitansi terhadap adanya perubahan suhu. Kapasitor kemudian di*annealing* di udara selama 12 jam pada suhu 700 ^oC untuk kristalisasi fasa. Sama dengan hasil sebelum *annealing*, lapisan tipis campuran Nb-Ti dengan rasio 30 % Nb_2O_5 masih menunjukkan nilai kapasitansi yang terbesar, meskipun ada sedikit perubahan nilai kapasitansi terhadap perubahan suhu. Dari hasil ini dapat dipertimbangkan bahwa lapisan tipis yang memiliki rasio 30% Nb_2O_5 dan 70% TiO_2 menunjukkan potensi paling bagus dengan nilai kapasitas yang terbesar dan sedikit perubahan terhadap perubahan suhu.

Kata kunci: Lapisan tipis Nb, Kapasitor, Fabrikasi lapisan tipis, Sifat elektrik, Kapasitansi, *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 tantalaum 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_2O_5 are well known examples that show metallic, semiconducting, and electrical phases, respectively.

Particularly, Nb_2O_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 scientiest 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_2O_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. Figure1 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 1×10^{-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 32mm × 10mm, pulse maximum energy of 450 mJ, maximum average output of 70W 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^o 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

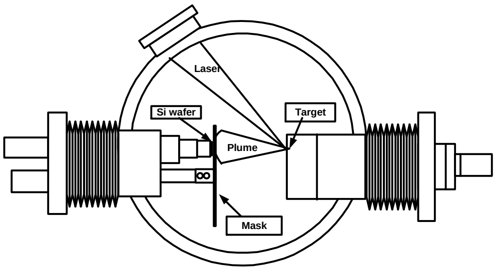

Figure 1. Schematic of Pulsed Laser Deposition apparatus

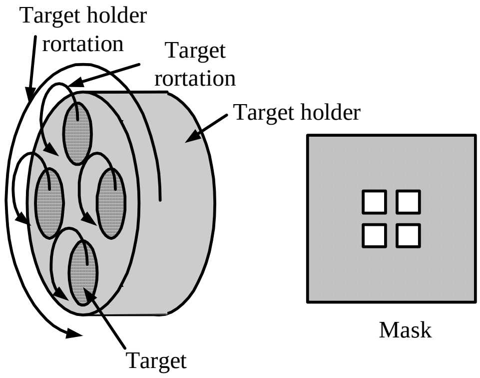

Figure 2. Schematic of target changer and mask

to prevent local heating. When depositing the particles generated by laser irradiation, a mask was placed in front of the deposition substrate to control the deposition geometry and to prevent the adhesion of droplet in the surface of film [12-13]. The shape of the mask shown in Figure 2. The presence of droplet was then adjusted by rotating the holder of the mask.

The thickness of thin film was measured by using a shape roughness measuring instrument. Composition analysis was carried out using X-ray diffraction. To produce single layer capacitor, the layer in the order of Pt//insulator (mixing of TiO_2 and Nb_2O_5)//Pt thin film was deposited on the Si(100) substrate (Pt was used as an electrode part). After producing one layer of capacitor, the capacitance and resistance value were then measured. Parameters for producing a single-layer film of TiO_2 and Nb_2O_5 are shown in Table 1.

Table 1. Experiment conditions of producing mixed thin film

Target	Pt	Nb_2O_5	TiO_2
Fluence	4.5 J/cm^2	4 J/cm^2	4 J/cm^2
Thickness	-	400 nm	400 nm
Total number of pulses	30000	47619	34783
Atmosphere	Ar 10^{-3} Pa	O_2 5 Pa	O_2 5 Pa
Substrate		SiO_2	
Temperature		600 °C	

The mixed thin film $(Nb_2O_5)_X.(TiO_2)_{1-X}$ were deposited by irradiating the laser alternately to the TiO_2 target and Nb_2O_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 cylce 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_2O_5 inside the thin film can be calculated by multiply 100 to (thickness of Nb_2O_5/200 nm). Table 2 shows each parameter when produce a mixed thin film.

Table 2. Parameter of producing $(Nb_2O_5)_X.(TiO_2)_{1-X}$ mixed thin film.

$(Nb_2O_5)_X$	0.1	0.3	0.5	0.7	0.9
Thickness			200nm		
Fluence			4 J/cm^2		
Nb_2O_5 shot value	6	20	41	50	65
TiO_2 shot value	40	34	30	16	5
Cycle value	394	358	290	330	347
Atmosphere			O_2 5Pa		

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.

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_2O_3 were observed. The peak of Pt as an electrode part was also identified.

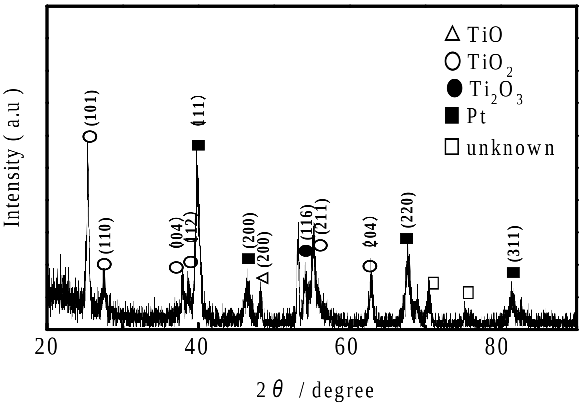

Figure 3. XRD patterns of pure TiO_2 thin film

Figure 4 shows the composition of single layer thin film with the thickness of about 400 nm, which has been deposited using Nb_2O_5 47619 shots of laser shot number. The peaks of Pt and Nb_2O_5 were confirmed clearly, and the peak of NbO was also identified. From the result of XRD many compounds of Nb-O at substrate temperatures was found. The temperature of substrate during the deposition of Nb_2O_5 was 600 °C, and under this temperature, the composition phase of Nb_2O_5 might be one of NbO, NbO_2 or Nb_2O_5. In the case of using TiO_2 target, the possibility of composition phase is TiO, TiO_2 and Ti_2O_3. In order to create the thin film that has the same composition phase with target, it is necessary to increase the binding or the ratio of oxygen during the process of deposition. It means that ratio of oxygen being mixed is a critical parameter.

The thickness of the cross-section of the thin film has shown in Figure 5, the deposition of

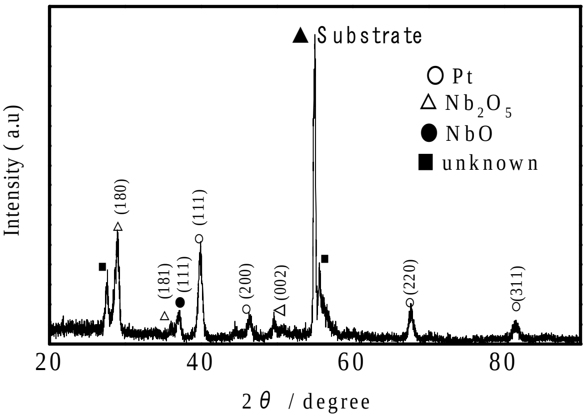

Figure 4. XRD patterns of pure Nb_2O_5 thin film

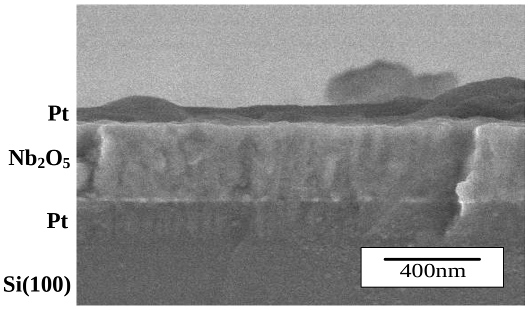

Figure 5. SEM photograph of pure Nb_2O_5 thin film.

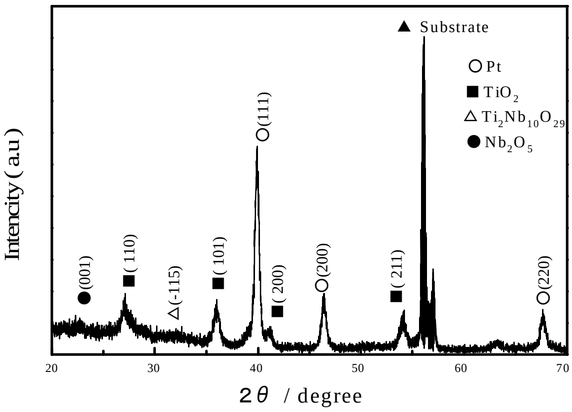

Figure 7. X-ray diffraction patterns of $(Nb_2O_5)_x(TiO_2)_{1-X}$ thin film.

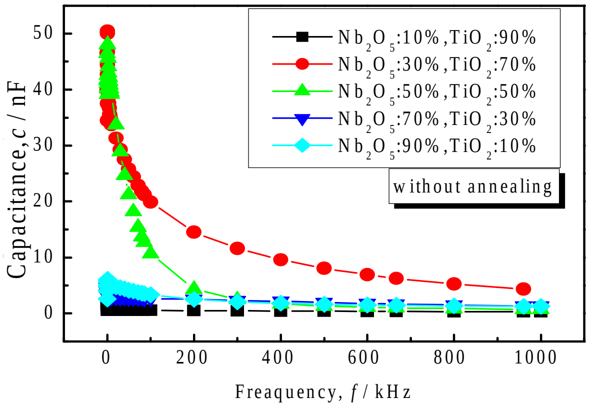

Figure 8. Capacitance of $(Nb_2O_5)_x.(TiO_2)_{1-x}$ thin film without anneal.

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_2O_5 and TiO_2 single thin film is shown in Figure 6. At low frequency, Nb_2O_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_2O_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_2O_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_2O_5 and Pt were also identified. Comparing with the result in Figure 3 and 4, after doping Nb_2O_5 to TiO_2 and annealing process, the film that only contain TiO_2, Nb_2O_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_2O_5 here can eliminate the generation of other composition, such as TiO, NbO and others.

The capacitance value of deposited $(Nb_2O_5)_X.(TiO_2)_{1-X}$ thin film that has fabricated by mixing Nb_2O_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_2O_5 inside the thin film from 10% until 90%. When the deposition of Nb_2O_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

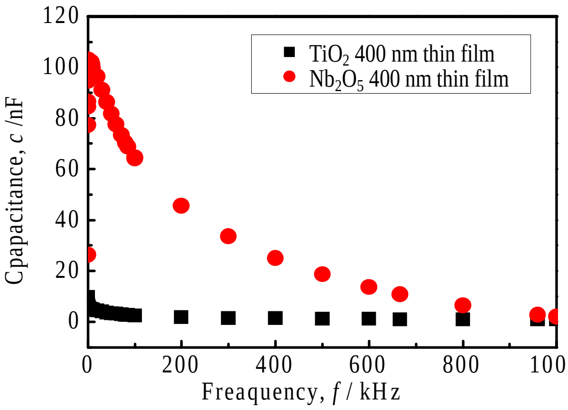

Figure 6. Comparison of the capacitance of Nb_2O_5 and TiO_2

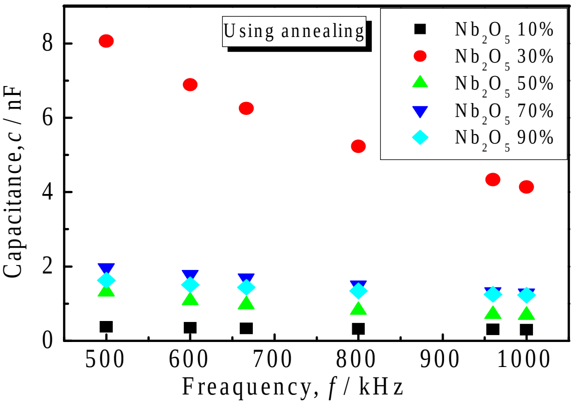

Figure 8. Capacitance of $(Nb_2O_5)_x.(TiO_2)_{1-x}$ thin film

value of capacitance at ratio of 30% Nb_2O_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_2O_5 was smallest, approximately more than 1/10 times in the case of 30% of Nb_2O_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_2O_5. The mixed Nb_2O_5-TiO_2 thin films with the ratio 30% of Nb_2O_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_2O_5 to TiO_2 is able to stabilize the capacitance changes with the increasing of frequency. It means Nb_2O_5 is potential to substitute the Tantalum for their using as electrode. However, the generation of other compound of Nb_2O_5 have to be surely controlled and be eliminated in the thin film production.

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