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Pulsed Laser Deposition of ZrO_2 Thin Films for Application in Microelectronic Devices

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The main aim of this research was to explore a relationships between main factors of deposition parameters and thermodynamical conditions, which determine the properties of ZrO_2 thin films prepared by reactive pulsed laser deposition (RPLD) on different substrates without the stage of post-deposition annealing. The structural, electrical and optical properties of grown films were investigated as a function of substrate deposition temperature and pressure of background gas atmosphere. On the basis of obtained results we have developed the method of manufacturing of thin films systems for application in microelectronic devices, which have been constructed on the base of ZrO_2 films. Besides, the main properties of manufactured systems have been measured.

Keywords: oxide thin film, pulsed laser deposition, oxygen pressure.

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I. Introduction

The oxide thin films are attracting an increasing interest from both material and electrical engineers/scientists because of their potential for use as the material with high dielectric characteristics for manufacturing of the film capacitors and as a buffer layer with high chemical stability at creation of multi-layers systems [1]. Recently, oxide materials with high dielectric parameters have been suggested as an alternative to the currently used SiO_2 gate dielectric for complementary application of metal oxide for using in semiconductor technology. Several oxide materials with high dielectric constant have been investigated as an alternative gate dielectric. However, their application is limited due to the interfacial reaction between dielectric materials and tradition microelectronic substrates, such as Si substrates, during the post annealing processes. Among the suggested materials, which are widely used in different opto- and microelectronic devices, the Zirconium Oxide (ZrO_2) thin films have many advantages, such as a high dielectric constant (15-22), a relatively large band gap (5.2-7.8 eV), good thermal stability and so on [2, 3]. In addition to the above advantages, ZrO_2 films are thermally stable with gate electrode materials during the deposition and following processes of treatment of gate electrode materials and they are compatible for mutual application in the semiconductor devices.

The integration of semiconductor technologies into the high-temperature superconducting (HTSC) oxide materials is a very important problem, because high-temperature annealing of HTSC films is not applicable for the technology of semiconductor materials. These problems can be overcame, when to use the buffer layers. It is know that the best results on the Si substrates can be achieved by using of the buffer layers, such as ZrO_2 thin films [4,5].

It is known various technologies, which can be used for fabrication of ZrO_2 films. But all suggested technologies include the stage of post-deposition annealing. Usually, optimum properties of ZrO_2 films have been achieved when they are deposited on a hot substrate and are annealed after deposition. Therefore, it is necessary to develop technology for deposition of ZrO_2 films at low temperature without considerable losses of their properties. Among these methods reactive pulsed laser deposition (RPLD) is the more perspective and supple method for preparation of ZrO_2 thin films, due to a high of growth rate, possibility of use of high pressure reactive gas ambience, simple means to drive of deposition processes. Hence, experimental definition of optimum parameters of RPLD for preparation of ZrO_2 films with good characteristics on heated or unheated substrate without post-deposition annealing is very important for practical applications.

We investigated the microstructure, electrical and optical properties of ZrO_2 films prepared by proposed method. As a result we defined main relationships between the deposition parameters of RPLD, thermodynamic conditions into deposition camera and basic properties of grown films. Besides, the study of a interaction between the grown films and substrates as a functional dependence of sputtering parameters and

Table.

Subject	Value
Target	Zr/ZrO2
Spot size on target	~2-3 mm
Energy density	Up to 1 J/cm2
Wavelength	1064 nm
Pulse duration	15 ns
Repetition rate	12-56 Hz
Deposition rate	From 0,001 up to 0,05 nm/shot
Target-substrate distance	20-30 mm
Target rotation	10 Hz
Pressure of reactive gas	up to 1000 mtorr
Substrate temperature	From 150^0C up to 450^0C

condensation conditions were carried out.

On the basis of grown films we manufactured the film system of metal-oxide-semiconductor as a capacitors for microelectronic application. Main parameters of prepared film systems were measured. Obtained results we used for growing of ZrO_2 films with very good parameters, as a buffer layers for epitaxial growth of high temperature superconductors films on semiconductor substrates and others.

II. Experiments

Q-switched Nd:YAG laser (with parameters 1064 nm, 15 ns, 0,1-1 J/cm^2) was used for ablation of target materials into reactive oxygen atmosphere. Ablated materials were condensed on the surface of different substrates at varied conditions. Films were deposited on melted quartz, (1102) sapphire plate, NaCl, (100) Si substrates at different amount of oxygen pressure (from dynamic vacuum up to 1000 mtorr) in wide range of substrate temperatures. The thicknesses of grown films were between 200-1200 nm. After standard procedure of cleaning of substrates, thin films of ZrO_2 were deposited on substrate surface by RPLD from two different targets (presyntezed ZrO_2 tablet or Zr plate with 99.9% purity) in oxygen background.

The ZrO_2 films were prepared by RPLD into a specially developed quasi closed reaction chamber (QCRC), which has been equipped with rotary pump and diffuse pump. The QCRC was previously pumped down to 10^{-6} torr or less. The oxygen was used as a reactive gas at the different amount of pressure. Only pure oxygen (99.99%) has been used as a reactive background gas in all experiments. The distance between the target and substrate surface was 20-30 mm. The temperature substrates were maintained in wide temperature range from 150^0C up to 450^0C. We used electroluminescent halogen lamps as a heaters. The position of point of absorption of laser pulse on the surface target during the ablation stage was changing by rotating of the target. The relevant parameters of growing process are listed in Table.

The quality of the films was investigated by X-ray diffraction, scanning electron microscopy and optical transmission spectroscopy. The spectral transmittance of grown films were investigated as a function of wavelength in the spectrum range 300-2000 nm. The resistivity of grown films was measured by four-point probe. The standard C-V measurements for produced structures were carried out by a computer-controlled impedance analyzer based on E7-9 unit, which was previously modernized. The structural, electrical and optical properties of grown films were studied as a function of deposition temperature and oxygen pressure.

III. Results and discussion

As a result of carried out examinations of growing conditions, we have established that at fabrication of ZrO_2 films by RPLD, the developed method demonstrates the higher abilities of reactivity. For example, we determined that the formation of ZrO_2 films with stoichiometric compound is a consequence of the ablation of pure Zr plate and condensation on surface substrate of ablated material, when oxygen pressure in QCRC is P = 20-60 mTorr. Detailed analysis of experimental investigation of deposition processes demonstrated that the formation mechanism of oxide films possesses a complex character, where a principal role plays the ionization and the excitation of sputtered material, oxidation processes on surface target and into generated plasma plume, on surface of growing film.

We have found that the reactive RPLD can be used for fabrication of ZrO_2 films with uniform thickness and homogeneous composition with very smooth surface. The growth rates of ZrO_2 films were studied by change

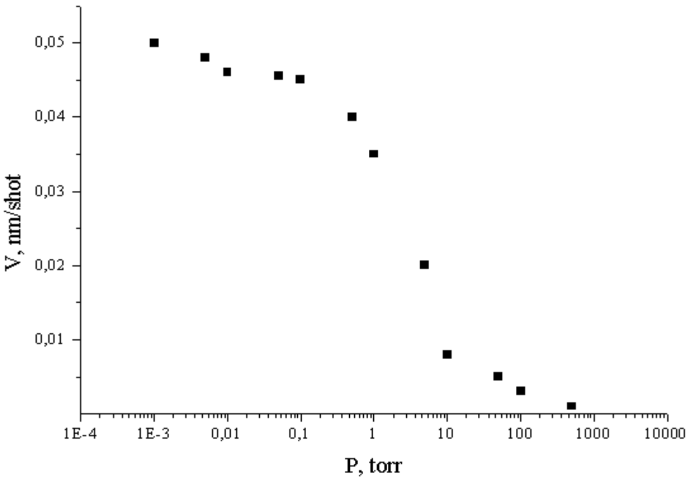

Fig. 1. Growth rates of ZrO_2 films as a function of oxygen pressure.

of deposition temperatures and oxygen pressure into deposition chamber. The experimental results indicated that the growth rates of ZrO_2 films were between 0.001–0.05 nm/shot at different amount of oxygen pressure. Obtained results are presented on Fig. 1.

The obtained results have shown that the growth rate depends on the geometrical configuration of the target and substrate surface, density power of laser radiation and substrate temperature. Electron microscope studies have shown that the films, grown at low substrate temperature ($T < 180°C$), are amorphous, but they can be crystallized by post-annealing in temperature range 500-800^{0}C at the oxygen pressure over 100 Torr. When the substrate temperature was increased to 200^{0}C, polycrystalline films were grown. The films deposited at the temperature between 200 and 250°C showed smooth polycrystalline surface with the grain size from 50 nm to 600 nm depending upon deposition parameters. Changing the substrate temperature up to 300^{0}C did not affect the polycrystalline nature of the films. The films with higher density and improved crystallinity were obtained at higher deposition temperatures. The ZrO_2 films, which were deposited at elevated temperatures up to 350^{0}C, were textured, and both the monoclinic and tetragonal phases exist in the film volume. X-ray diffraction spectral analysis of crystalline structures of ZrO_2 films, which have been prepared by RPLD on Si-substrates at temperature 350^{0}C, demonstrated only two different diffraction peaks. Peaks, which are located at $2\theta = 28.3^o$ and $2\theta = 30.5^o$, indicated that the monoclinic and cubic phases of ZrO_2 material were formed. We established that the cubic form is stable when thickness of grown films were below 0.10 μm. Existence of both phases specifies, that the size of a mosaic block overlaps this amplitude. It was established that the grain size of grown films is practically unchangeable at decreasing of the oxygen pressure.

Studies of electrical parameters of ZrO_2 films, which have been grown at different deposition conditions, were carried out. We demonstrated that the good electrical properties of grown films could be achieved only if the content of oxygen was optimized. Analysis of obtained results has shown that the electrical properties of grown films possess a high sensitivity to both the exact ratio of metal elements and the exact oxygen content. It was confirmed by fact, that the electrical resistivity (R) was strongly depended on oxygen pressure during the deposition stage. The ZrO_2 films with the low values of electrical resistivity (about 10^{-2} Ohm/cm) were grown when the oxygen pressure was < 0.01 mTorr. The high values of electrical resistivity (R~500 Ohm/cm) was achieved in films in case, when the oxygen pressure was > 100 mTorr. The influence of oxygen pressure on the resistivity of ZrO_2 films, which were grown at the different temperatures of substrates, are presented on Fig. 2. Results shown on Fig. 2 testify that the resistivity of ZrO_2 films increases with increasing of oxygen pressure. We observed the significant increasing of R when substrate temperature was above 500^{0}C.

For measuring of transmittance, films have been deposited on sapphire substrate at different pressure of oxygen, when substrate temperature was 350^{0}C. Typical transmittance spectra as a function of amount of oxygen pressure were measured at the room temperature and are presented on Fig. 3. These measurements demonstrate that the transmittance in the visible region for grown films increases at the increasing of oxygen pressure from 0.01mTorr up to 1000 mTorr. Obtained results indicated, that film transmittance is strongly determined by the amount of oxygen stoichiometry in the films material. Analysis of obtained results testify that ZrO_2 films with resistivity about 1-10 Ohm/cm and transmittance with > 90% can be prepared by RPLD at the oxygen pressure 500-600 mTorr and substrate temperature 380-400^{0}C. As a result of analysis of measured experimental values, which are show on Fig. 2 and Fig. 3, we have established that the higher oxygen pressure tends to give a high

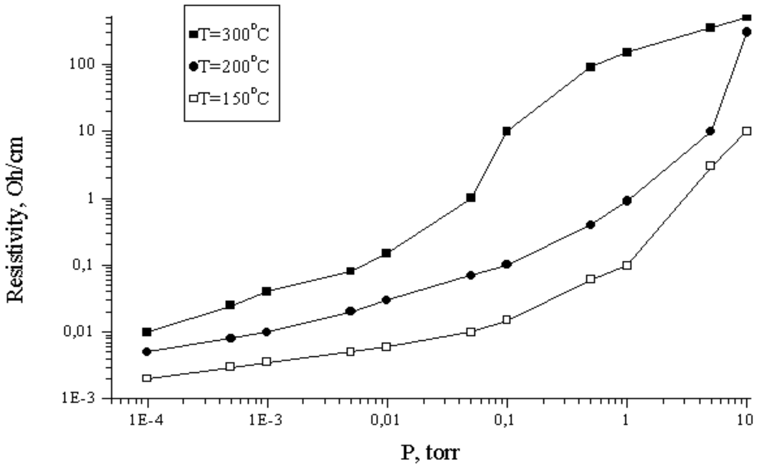

Fig. 2. The influence of oxygen pressure on the resistivity of ZrO_2 films prepared by RPLD at different substrate temperatures.

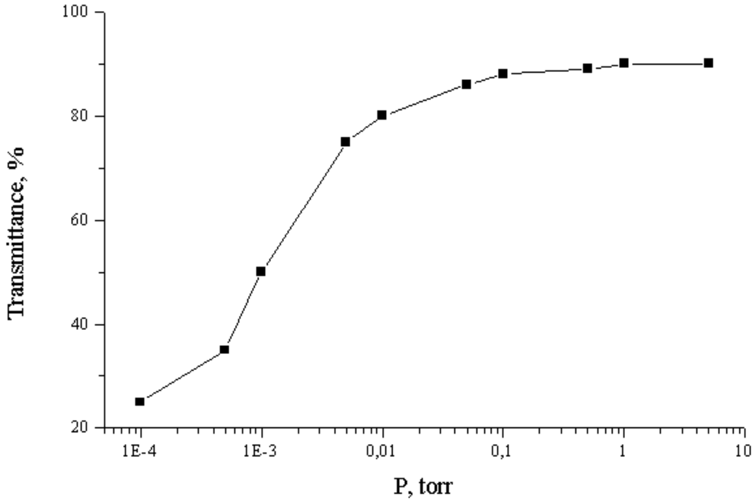

Fig 3. Measured transmittance of ZrO_2 films deposited on sapphire substrate at different pressure of oxygen.

transparent films with high resistivity. We guess that the high resistivity of films, which have been deposited at a higher oxygen pressure, is a possible result of better stoichiometry of film material. Our opinion is confirmed by a fact, that the films which have been grown at lower oxygen pressure, demonstrated the low value of transmittance. It is known that the lower film transmittance testifies about the more deficiency of oxygen in the volume of film material.

We've made the attempt to explore the possible use of ZrO_2 thin films in standard metal-oxide-semiconductor (MOS) technologies for manufacture of capacitors, with use a metal as the gate electrode. After the deposition of ZrO_2 films on surface of Si substrates, the electrode material in form of thin film, was deposited by PLD in high vacuum. We used the aluminum (Al), as an electrode material. Capacitor structure with size from 78.5×10^{-6} cm^2 up to 3.14×10^{-4} cm^2 was produced by using a set of special masks, which have been placed near the surface of substrate. These structures were constructed on the base of ZrO_2 films with thickness of 500 nm and Al films with thickness over 1-µm, as the top electrodes. They have served as the standard devices to examine insulator properties of ZrO_2 films. Finally, chromium or gold films with thickness of 1-µm were deposited by PLD into high vacuum on the backside of all samples to form a good ohmic contact to the substrates. The main properties of manufactured systems

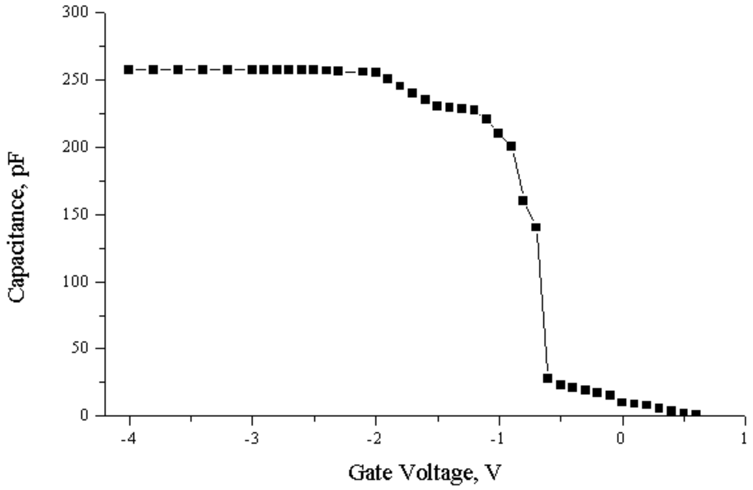

Fig. 4. Typical C-V curve of Al-ZrO_2-Si-Au capacitor.

were examined as a function of voltage. The gate voltage was swept from the negative to positive bias and back to negative bias to exclude any hysteresis effects. The set of C-V curves, which have been measured along the voltage axis, is shown on the Fig. 4.

The dielectric constant of the ZrO_2 film was calculated from the maximum capacitance (accumulation region) of the C-V curves, according to the relationship:

$$C = \frac{\varepsilon_0 \varepsilon \ A}{d}, \qquad (1.1)$$

where ε is the relative dielectric constant, ε_0 is the dielectric constant, d is the oxide film thickness and A is the square of the capacitor system surface. For experimental samples, which have been constructed on the base of ZrO_2 film prepared and gate electrode layer prepared, we determined that the relative dielectric constant for ZrO_2 films was as high as 18 ± 0.5.

In addition, we propose the developed method for manufacture of ZrO_2 buffer films, as a buffer layer, for Y-Ba-Cu-O/ZrO_2/Si systems. In this case the Y-Ba-Cu-O films with thickness up to 1 μm, were deposited on the Si substrates, which previously have been covered by the ZrO_2 buffer layers. These systems possess the high-temperature superconductor characteristics. The prepared film systems demonstrated a superconductivity with temperature of superconductive transition beginning from 82 K and with an end-point of temperature of superconductive transition to 60 K at the temperature of liquid nitrogen.

IV. Conclusions

The ZrO_2 films with high transmittance, good conductivity and high chemical stability for application in microelectronic devices and related high-technology applications were prepared by the RPLD without post-deposition annealing. The crystalline structure of grown films was determined by substrate temperature. It is established that the effect of oxygen pressure on the resistivity and transmittance of grown films is independent and determinative factor. We produced the Al-ZrO_2-Si film systems as the thin film capacitors, which have been based on the relative simplicity of manufacturing of Al electrodes, and ZrO_2 dielectric films by PLD technology. Obtained results can be used as a base for application of the ZrO_2 thin films into microelectronic material science as high dielectric constant insulators, buffer layers for epitaxial growth of high temperature superconductors films on semiconductor substrates and others.

[1] K.S. Krisch, J.D. Bude, L. Manchanda. Gate Capacitance Attenuation in MOS Devices with Thin Gate Dielectrics // *IEEE Electron Device Letters*, **11**(17), pp. 521-524 (1996).

[2] S. Chatterjeea, S.K. Samantaa, H.D. Banerjeeb and C.K. Maiti. Electrical properties of stacked gate dielectric (SiO_2/ZrO_2) deposited on strained SiGe layers // *Thin Solid Films,* (422), pp. 33-38 (2002).

[3] Jung-Ho Yoo, Seok-Woo Nam, Suheun Nam, Dae-Hong Ko, Ja-Hum Ku, Cheol-Woong Yang. Physical and Electrical Characteristics of ZrO_2 Thin Films as a Promising Gate Dielectrics // *Journal of Electronic Materials*, **7**(31), X5, (2002).

[4] T. Venkatesan, E.W. Chase, Wu X.D. Superconducting $Y_1Ba_2Cu_3O_{7-x}$ films on Si // *Appl. Phys. Lett.,* (53), pp. 243-245 (1988).

[5] S. Witanachiki, H.S. Kwok, S. Patel, D.T. Shaw. As-deposited Y-Ba-Cu-O superconducting films on silicon at 400 C // *Appl. Phys. Lett*, **6**(54), pp. 578-580 (1989).

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Опромінення імпульсним лазером тонких плівок ZrO_2 для використання у приладах мікроелектроніки

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Головна мета цієї роботи – дослідити зв’язок між основними коефіцієнтами параметрів опромінення і термодинамічних умов, які визначають властивості тонких плівок ZrO_2, утворених імпульсним лазером на різних підкладинках без подальшого відпаду. Досліджено структурні, електричні і оптичні властивості вирощених плівок, як функції температури опромінення підкладинки і атмосферного тиску фону. На підставі одержаних результатів розроблено метод виготовлення систем тонких плівок для використання в приладах мікроелектроніки, розроблених на основі плівок ZrO_2. Крім того, виміряно основні властивості виготовлених систем.