The research on optical method for determining amorphous La$_2$O$_3$forbidden band width

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Abstract: *The feature size of semiconductor devices is getting smaller, and the thickness of the traditional SiO$_2$ layer is close to the limit of quantum tunneling under the progress of microelectronics technology. Therefore, the study of high performance of high-k materials is very important. The forbidden band width is an important parameter to study rare earth oxides as high-k gate dielectrics, and larger of forbidden band width, smaller of leakage current. In this paper, La$_2$O$_3$ is grown on Si(100) and quartz substrate on ultrahigh vacuum magnetron sputtering equipment, and the forbidden band width of La$_2$O$_3$ is obtained through optical path proposed by Tauc et al. The reliability of measuring La$_2$O$_3$ forbidden band width is verified by XPS. The experimental results show that the forbidden band width of La$_2$O$_3$ measured by optical method is 5.15±0.2eV, and forbidden band width of La$_2$O$_3$ measured by XPS is 5.10±0.15eV, the results of two ways are similar.*
Keywords: *Feature size, high-k gate dielectrics, XPS, forbidden band width.*

I.   Introduction

With the rapid development of the semiconductor industry, the feature size of the devices always follows Moore's law. That means the feature size of the devices is gradually decreasing, and the quality and function of IC(Integrated circuit) is improving greatly. At present, improving system performance of the integrated circuit mainly by reducing the size of devices, and it is related to the physical thickness of CMOS gate dielectrics. Once the thickness of the equivalent SiO$_2$ gate dielectrics is less than 1nm, the edge value of quantum tunnel breakdown will be achieved. Since the development of semiconductor industry, the thickness of SiO$_2$ gate dielectrics has been reduced to the limit of electrons tunneling breakdown. If we reduce the thickness of gate oxides later, it will lead to a sharp rise in leakage and power consumption, resulting in devices failure.

Although 14Å or even smaller thickness of SiO$_2$ insulation layer is available, the leakage current will increase by 5 times for every 1Å of reduction of the SiO$_2$ gate dielectrics, which make the use of SiO$_2$ gate dielectrics in the future difficultly. More importantly, many research groups have studied the ultimate thickness of SiO$_2$, the physical thickness of the limit value is 7Å[1]. When the thickness of SiO$_2$ less than 7Å, it will not be able to guarantee original insulating properties, which means it will lose its status as a reliable gate dielectric materials[2-3]. In order to overcome the difficulty of gate dielectrics, we use high-k(the value of *k* is larger than the dielectric constant of SiO$_2$) materials instead of SiO$_2$[4-6].

However, the size of *k* is not the only standard to examine the merits and demerits of high-k materials. Research shows the forbidden band width also plays a decisive role in two ways, one is the suppression of electron and hole tunneling probability, the other is providing a barrier height. Therefore, the measurement of forbidden band width becomes a necessary part of studying on the rare earth oxides as high-k gate dielectrics. Rare-earth metal oxides have many advantages such as high dielectric constant(~10-30) and wide forbidden band width(~5-7 eV) [7-9]. It has become an excellent materials for high-k gate dielectrics, especially La$_2$O$_3$ as the most promising high-k gate dielectric materials in rare earth oxides.So the measurement of forbidden band width is a necessary part of the study of rare earth oxides as high-k gate dielectric materials. The research on the forbidden band width of semiconductor materials is generally Tauc method, which is measured by ultraviolet visible spectrophotometer. The main process is to measure the transmission spectrum of the samples grown on the quartz substrate, and then use the Tauc formula to obtain the forbidden band width.

Several researches about determining forbidden band width of rare earth oxides have been reported[10-11]. S.A.Chambers et al. suggested that the band gap width of rare earth oxides can be determined by the difference of energy between the O 1s peak of X-ray Photoelectron Spectroscopy(XPS) and the starting positions of their energy loss peak[10]. Later, in another report, S. Miyazaki adopted XPS to measure the forbidden band width of some high-k gate dielectrics[11]. However, there is still a lack of verification to measure forbidden bandwidth of rare earth oxides.

In this paper, La$_2$O$_3$ is grown on Si(100) by ultra-high vacuum magnetron sputtering equipment, and

La$_2$O$_3$ forbidden band width is obtained by the optical method proposed by Tauc et al, XPS is used to verify the measurement of La$_2$O$_3$ forbidden band width reliability.

II.   Preparation technology and condition of La$_2$O$_3$ thin films

2.1 Preparation technology

There are many ways to grow thin films, such as physical vapor deposition(PVD), chemical vapor deposition(CVD) and magnetron sputtering technology[12]. In all kinds of thin films deposition techniques, magnetron sputtering technology has been widely used because of low temperature and high speed[13].
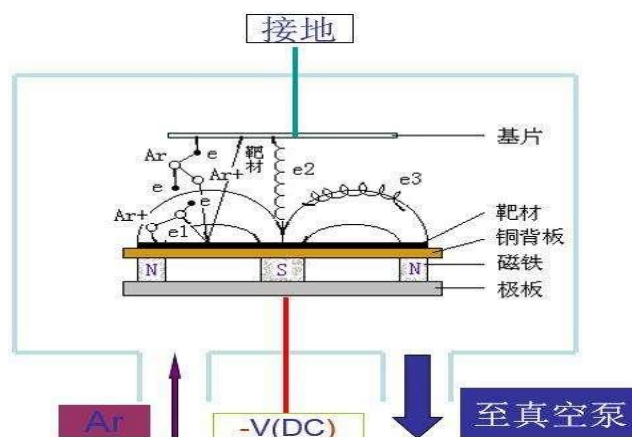

Fig. 1 The principle of magnetron sputtering technology

The principle of magnetron sputtering technology is shown in Fig.1. We fill vacuum chamber with Ar, electrons collide with Ar in the process of accelerating toward the substrate under the action of the electric field, and then Ar ionizes to generate Ar$^+$ and electrons. After that, electrons accelerates toward the substrate, Ar$^+$ accelerates toward the cathode sputtering target and bombards the target surface with high energy to cause sputtering of the target materials, the neutral target atoms (or molecules) are deposited on the substrate to form films. In short, magnetic field changes the direction of electronic motion, binds and prolongs the motion path of electrons. As a result, it enhancing the ionization probability of electrons and effectively utilizing the energy of electrons.
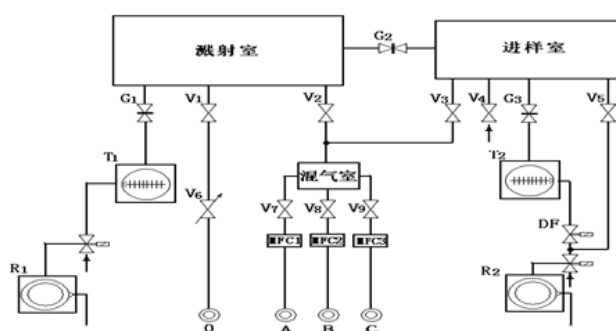

Fig. 2 Structure diagram of ultra-high vacuum magnetron sputtering instrument

The magnetron sputtering apparatus consists of a control system, a mechanical system and a cooling system, as is shown in Fig. 2. The control system consists of two operating consoles. A real-time monitoring and control of the films preparation process of various data, such as vacuum cavity vacuum degree, the size of the work pressure, the molecular pump and mechanical pump working conditions, and other specific conditions. The other console is mainly used for working condition control during sputtering, such as the type of sputtering power supply, the setting and control of the sputtering power, the size of the positive and negative bias pressure. Mechanical system is mainly used to obtain high vacuum and complete the mechanical work of the components, through the system of molecular pump and mechanical pump work, the vacuum cavity inside the air out, so that its vacuum degree to meet the requirements. At the same time, the other parts of the mechanical system also complete the vacuum chamber switch, the adjustment of the substrate position. The vacuum system completes

the real-time measurement of the vacuum chamber and provides the necessary conditions for preparing the films. The minimum vacuum of the test is generally greater than 10^{-4}Pa, and the pressure is generally required from 0.1Pa to 10Pa. The cooling water circulation system is mainly to prevent the mechanical pump and the high-speed operation of the molecular pump cause the overheating of the machine, but also to ensure that the thin films preparation process required room temperature conditions.

2.2 Preparation condition
La₂O₃ is grown on Si(100) by magnetron sputtering apparatus(JGP500D1) at room temperature, and we use P-Si with 2-10Ω. In order to remove the effects of substrate and other sources of contamination, so as to make the thin films grow, we should clean the substrate thoroughly. The specific processing process is as follows:
1. Rinse deionized water
2. Ultrasonic 10 minutes for acetone
3. Rinse deionized water
4. Ultrasonic 10 minutes for deionized water
5. Ultrasound 5 minutes for alcohol
6. Rinse deionized water
7. Ultrasound 5 minutes for alcohol
8. Etching for 30 seconds of 10% HF
9. Nitrogen drying

Wash the substrate and seal it in place where the vacuum chamber is fixed. The vacuum of the thin films growth chamber reaches approximately 0.00027Pa and filled with Ar, control the pressure of sputtering about 1Pa. After the working pressure is stabilized, the sputtering target (La₂O₃ ceramic target with purity of 99.99%) is sputtered and the thin films is deposited on the substrate before the 10-15min is sputtered. In order to obtain a high quality thin films, annealing in O_2 at 300°C for 30 min after deposition. At the same time, in order to obtain accurate forbidden band width, La₂O₃ thin films on quartz substrate for optical test under the same growth condition.

III. Experiment and analysis
3.1 Optical method for measuring forbidden bandwidth of La₂O₃
The measurement of forbidden band width of La₂O₃ by optical method is based on the method which put forward by Tauc et al[14], and it has been widely used. In the experiment, we test La₂O₃ on the quartz substrate by UV-2550. We choose the UV-visible light source in the wavelength range of 150nm to 750nm, and collect the transmission and absorption spectra of the sample to analyze and calculate the specific forbidden band width[15-16]. It is reported that there is a connection between the absorption coefficient of UV-visible absorption spectrum and forbidden band width[17]

$$(\alpha h v)^2 = C(h v - E_g) \tag{1}$$

In the above formula, α is a absorption coefficient of ultraviolet spectrum, *hv* is a incident photon energy, C is a constant. In the meantime, we can measure the transmittance of the thin films that grow on the quartz substrate to obtain the specific absorption coefficients by combining the following equation[18]

$$\alpha = -\ln(T)/d \tag{2}$$

where *d* is the thickness of the thin films and given by the test of ellipsometry. The corresponding absorption coefficient is calculated with equation(2) and then make a figure of $(\alpha h v)^2$ relative to *hv*. Combined with equation(1), it is found that when $(\alpha h v)^2$ is 0, E_g is equal to *hv*. Therefore, we make a linear extrapolation of the changes of the obtained spectra to $(\alpha h v)^2$ to 0, and obtainE_g of the materials.
As shown in Fig.3, ultraviolet visible wavelength between 230nm to320nm, the transmission rate increases dramatically, and band transmission rate is close to 1 after that, it shows that between the wavelength at 230nm to 320nm light energy is absorbed. We use equation(2) to transform graph data into drawing, and the result is shown in the inline diagram of Fig.3. The linear extrapolation of the $(\alpha h v)^2$-*hv* curve shows that the forbidden band width of La₂O₃ is 5.15±0.2eV, the error of 0.2eV comes from the test.
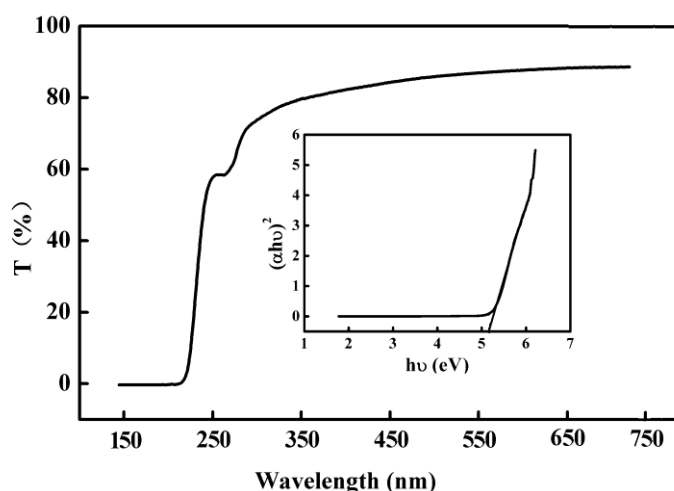
Fig. 3 UV transmission spectra of La$_2$O$_3$/quartz substrate films

3.2 XPS for measuring forbidden bandwidth of La$_2$O$_3$

Next, we use XPS to calculate the forbidden band width of La$_2$O$_3$. The method of determining the forbidden band width of high-k gate dielectrics by XPS spectroscopy has also been proved to be a successful and effective method. According to the principle of XPS mentioned above, we know that there are two types of energy loss during the escape process of X light, one is plasma excitation, the other is E_V excited by electrons and then E_C. For these reasons,$E_g$can be obtained from the energy difference between the O 1s peak on the XPS spectrum and the beginning of its energy loss peak.

In order to avoid the influence of the surface impurities on the test, we used the Ar+ etching method to make the sample surface of the mask to splash down about 2nm to collect the data. At the same time, in order to eliminate the interference of the substrate signal to the test result, a grazing incidence is used in the testing process, and the photoelectron take-off angle is 150°. Fig.4 shows the XPS spectra of the O 1s and O 1s energy loss peak of La$_2$O$_3$ thin films.

As shown in Fig.4, the process of determining the starting position of the O 1s energy loss using the linear extrapolation method. Combined with O 1s peak, it can calculate the difference between O 1s peak and the starting position of its energy loss peak, that means the forbidden band width value of La$_2$O$_3$ is 5.10±0.15eV, and the relatively larger error is 0.15eV that is due to the wide and the weak energy loss peak strength of O 1s.
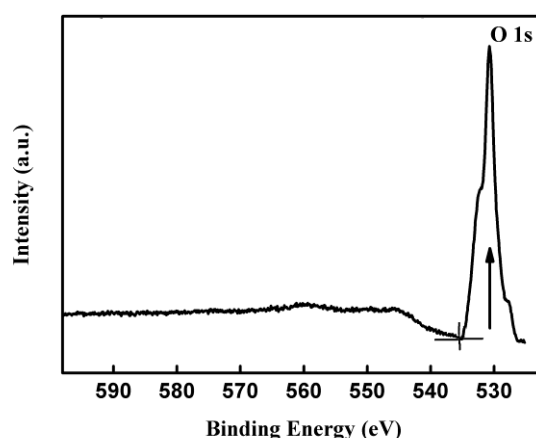

Fig. 4 XPS spectra of O 1s and O 1s energy loss of amorphous La$_2$O$_3$ films

In the end, table 1 shows the forbidden band width of La$_2$O$_3$ obtained by two methods, the result of XPS is basically the same as the result of optical method. Therefore, it is feasible to measure the forbidden forbidden band width of the rare earth oxides by optical method within the allowable error range.

Table 1 The forbidden band width of La$_2$O$_3$ obtained by two methods

materials	methods	
	optical(Eg)	XPS (Eg)
La$_2$O$_3$	5.15±0.2 eV	5.10±0.15 eV

IV.   Conclusion

The La$_2$O$_3$thin filmsis grown on Si (100) by ultra high vacuum magnetron sputtering equipment, and the filmsis tested after annealing. We also make a detailed description, its characterization technology is mainly XPS and UV-visible technology. Through analysis, we make a conclude.

The optical method is used to analyze the UV-visible light transmission spectrum of La$_2$O$_3$ films, and the width of the forbidden band width of La$_2$O$_3$ is 5.15±0.2eV. The XPS method is used to analyze the O 1s and O 1s energy loss spectra of La$_2$O$_3$ films, and the forbidden band widthis 5.10±0.15eV. It can be proved that the forbidden band width of La$_2$O$_3$ is accurate, and two methods to measure the forbidden band width of high-k gate dielectrics are reliable.

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