

Transparent SiO_xCyHz Barrier Film Prepared by Roll to Roll PECVD

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Abstract: This paper uses plasma-enhanced chemical vapor deposition (PECVD) to successfully fabricate silicon oxide films on silicon dioxide substrates for supporting layers of uncooled infrared focal plane array microbridge structures. In this paper, the thickness, refractive index, growth rate, and other parameters of the films were measured using the XP-2 step meter and ellipsometer. At the same time, atomic force microscopy (AFM) was used to study the surface morphology of the films. The experimental results show that deposition temperature and ICP power are the main factors affecting the growth rate of thin films. Deposition temperature is a crucial factor affecting the surface morphology of thin films.

1. Introduction

Energy, information, and materials are the three pillars of contemporary civilization, and materials are the carrier and support of energy and information, without which the conversion, transmission, and utilization of energy and information cannot be carried out. As an essential branch of many classifications of materials, thin-film materials represented by silicon thin films have penetrated various necessary fields of modern science and technology and the national economy. They are widely used in aerospace, medicine, energy, transportation, and communication, information, and home electronics: consumer products and other aspects of meeting people's growing needs. In the fields of sensors, thin-film transistors, thin-film solar cells, etc., the application of silicon thin films is of particular interest, and new progress has been made at home and abroad. At present, thin-film materials such as silicon film, as a vital new force in the entire material discipline and industry, have become an essential scientific and technological growth point for many countries in today's information and knowledge economy era and promote the continuous development of society.

As early as the mid-17th century, people began to study thin films. In 1650, R. Boye et al. observed the coherent color pattern produced by the liquid film on the liquid surface. Subsequently, various methods and means for preparing thin films were born one after another. In 1850, M. Faraday invented the method of electroplating to prepare thin films; in 1852, W. Grove invented the sputtering deposition method of glow discharge, and T. A. Edison invented the method of physical evaporation to prepare thin films by evaporating materials by energized wires at the end of the 19th century. Although thin-film technology continues to develop, the application of thin-film was initially limited to anti-corrosion and the manufacture of mirrors. Due to the backwardness of the

early technology, the obtained films have poor repeatability, thus limiting the application of the films. The repeatability of the thin film was significantly improved after the vacuum system, and detection systems (such as electron microscopy, low energy electron diffraction, and other surface analysis techniques) for preparing thin films had made significant progress. There are many ways to prepare thin films. The rise of the electronics and information industries, especially in the large-scale fabrication of printed circuits and the miniaturization of integrated circuits, thin-film materials, and thin-film technology have shown their unique advantages. Today, the research and development of a new material often start with the synthesis and preparation of thin films of this new material. Similarly, in the high-tech industry, thin-film technology, and thin-film materials also occupy an important position. Today, thin-film materials are developing in the direction of comprehensive, intelligent, composite, environment-friendly, energy-saving and long-lived, and nano-sized, which will indeed promote and promote the development of the entire material.

Organic electronics and optical devices develop rapidly, but packaging materials and packaging methods with high gas barrier properties are still tricky problems hindering their development. Polymer films are favored by people because of their lightweight and low cost and are widely used in packaging, aerospace, thin-film solar cells, and optical displays. However, due to the inherent disorder and non-dense structural characteristics of polymer chains, the film materials' barrier properties are challenging to meet the increasingly high development requirements [1]. Applying an overcoat is the most effective way to improve the barrier properties of thin films, and the coating materials that can be selected include organic and inorganic materials. The barrier properties of organic materials, such as polyvinyl alcohol, are greatly affected by the environment; inorganic materials, such as aluminum oxide and silicon oxide, have stable performance and are the most commonly used film coating materials. $\text{SiO}_x\text{C}_y\text{H}_z$ thin films have low thermal conductivity, high mechanical strength, and minor stress, and also have good micromachining properties, which are regarded as ideal materials for the support layer of microbridge structures [2]. The performance of the silicon oxide film directly affects the performance of the microbridge structure, so how to prepare high-quality silicon oxide film has become the focus of research. The authors used a pair-roll structure PECVD system to deposit high-barrier $\text{SiO}_x\text{C}_y\text{H}_z$ transparent films on polymer substrates. It has tremendous application potential in the development of the barrier film industry.

2. Experimental Design

2.1. Roll-to-roll PECVD deposition system

The principle of the discharge structure of the PECVD coating machine is shown in Figure 1. The system uses a counter electrode roll structure to tension the base film on the roll surface for continuous winding coating [3]. One of the essential features of this new type of PECVD coating equipment is that the medium frequency AC power is applied to the twin rolls, in which the non-rotating magnet system is assembled to produce an elliptical magnetically enhanced discharge area on the surface of the pair of rolls.



Figure 1: MF-PECVD coating device diagram

Oxygen/silicon ether (O₂/HMDSO) mixture is used as the process gas. Due to the reaction consumption of HMDSO, a gas gradient distribution with a high monomer above and a low monomer below is formed from the gas distribution port to the gas extraction port. The inside of the electrode roller is an entirely symmetrical magnetic system; the magnetic systems of the two rollers are opposite, the plasma is confined between the pair of rollers by the magnetic field, and the AC magnetron discharge helps excite the plasma [4]. The surface of the deposition roller is covered with an insulating organic base film, but the frequency of the intermediate frequency discharge is sufficient to penetrate the polymer base film to achieve glow discharge. At the same time, the process gas for deposition is distributed to the area between the rollers, and the source gas is decomposed, ionized, excited by the plasma, and adsorbed on the organic base film on the surface of the electrode roller to grow a thin film (Figure 2)..

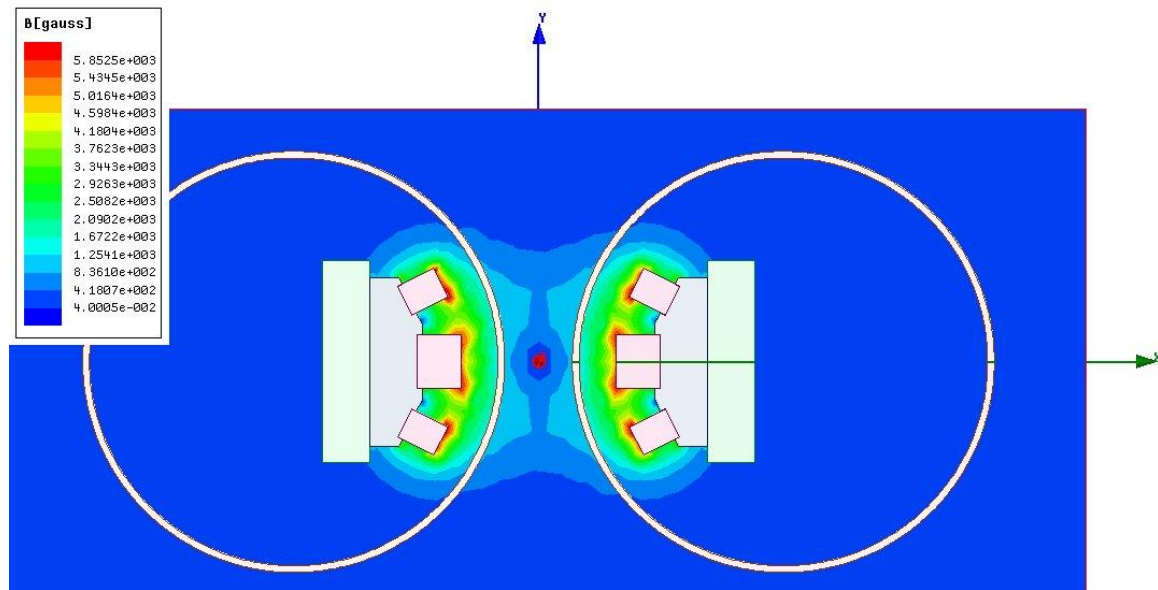
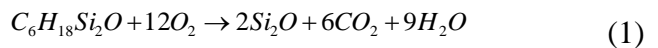


Figure 2: Schematic diagram of the simulation of the magnetic field distribution of the pair of electrodes

Due to the design of the system structure, the middle of the counter electrode is the position of the gas distribution plate, and the middle of the lower counter electrode is the opening position of the air pump group. When the O₂/HMDSO mixture is used as the process gas, the molecular weight of the HMDSO monomer is more extensive, and the speed is slower than that of the O₂ movement [5]. A composite film with a gradient distribution of high oxygen above the high monomer is formed from the gas port to the gas suction port. Its chemical reaction formula is:



2.2. Deposition process parameter setting

The experiment adopts the silicon wafer (as the substrate, wherein the thickness of the SiO₂ layer is about 50nm after thermal oxidation treatment [6]). Before the experiment, the substrate is ultrasonically cleaned for 10min with toluene, acetone and alcohol in turn, and then the cleaned sample is cleaned with Ar plasma. Clean for 10min for standby use. The background vacuum degree of the reaction chamber is better than 3×10^{-3} Pa. The preparation process parameters are shown in Table 1.

Table 1: Experimental Parameters of PECVD Principle Prototype Coating

Parameter	Parameter Variation range
Oxygen-to-HMDS Of low ratio	0.5-20
Reactor pressure	1-10Pa
MF power	200-2000W
Winding speed	0.5-5m/min

2.3. Preparation process

The crystalline state of the thin film was tested with a D/MAX-3B X-ray diffractometer from Rigaku Corporation; the bond structure of the thin film was analyzed with Fourier transform infrared spectroscopy (FTIR); the surface morphology of the thin film was observed with a SPA-400 atomic force microscope (AFM). The thickness and uniformity of the film were tested with the XP-2 step meter; the stress of the film was tested with the GBS6341 electronic film stress distribution tester; the temperature resistance of the film was tested with the RTP-500 rapid annealing furnace. Its process flow chart is shown in Figure 3:

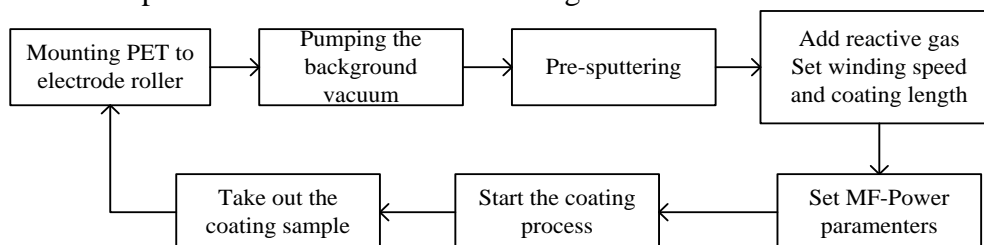


Figure 3: Process flow of composite membrane preparation

3. Results

3.1. Influence of plate spacing on film properties

when capacitively coupled radio frequency PECVD is working, radiofrequency voltage is applied to two flat electrodes placed opposite each other, and a reactive gas is passed between them to generate plasma to realize the deposition of thin films on the substrate. In this device, the plate spacing also has an important influence on the properties of the prepared films. Figure 4 shows the effect of the electrode spacing on the refractive index, thickness, and thickness uniformity of the silicon oxide film when the oxygen/silicon ether (O₂/HMDSO) is 0.46, and other parameters remain unchanged. It can be seen from Figure 4 that in the case of oxygen/silicon ether (O₂/HMDSO) of 0.46, the electrode spacing is proportional to the thickness of the silicon oxide film. In contrast, the film thickness is inversely proportional to the electrode spacing in conventional industrial production. This unique phenomenon may be related to the oxygen/silyl ether (O₂/HMDSO) ratio in this paper. At the same time, with the increase of the plate spacing, the thickness uniformity of the prepared film becomes worse, and the refractive index decreases accordingly, which may be because the increase of the plate spacing affects the distribution of the electric field in the reaction chamber, which harms the thickness of the film.

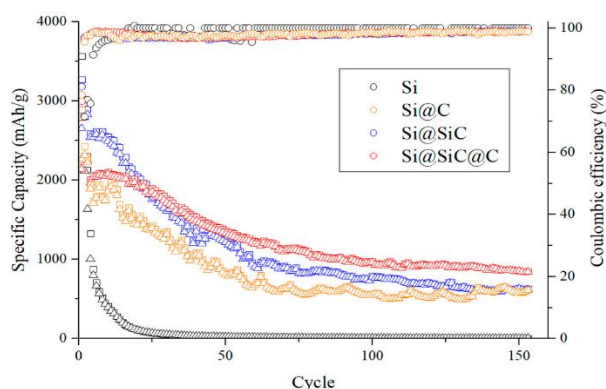


Figure 4: Relationship between plate spacing (Spacing) and silicon oxide film performance

3.2. Influence of chamber air pressure on deposition results

Figure 5 shows the effect of chamber air pressure on the growth rate of thin film deposition. It can be seen from Figure 5 that as the gas pressure increases, the deposition rate of the film increases and then decreases. When the initial cavity pressure can ensure that the plasma can maintain a stable glow discharge, with the increase of cavity pressure, the probability of collision between gas molecules increases, which increases the probability of collision between the reactive gases activated by the plasma and further improves the growth rate of the thin film. However, the excessively high gas pressure will make it difficult to discharge the reaction waste gas, and the problems such as the increase of the discharge amount of the reaction products will reduce the probability of plasma collision and eventually lead to the slowing down or even the decline of the growth rate of the film. At the same time, the increased non-uniformity of the film will also adversely affect the sidewalls of the cavity. It is therefore not recommended to perform deposition experiments under high-pressure conditions.

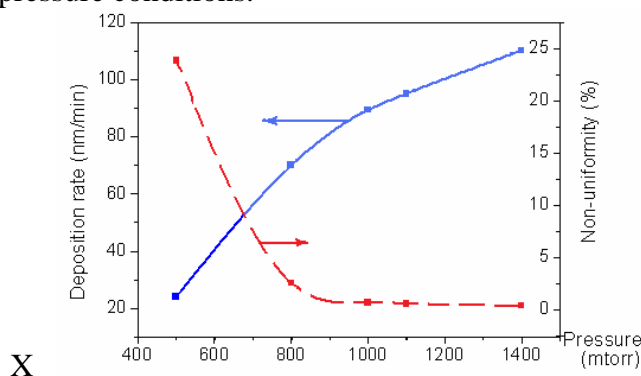


Figure 5: Influence of chamber air pressure on deposition results

3.3. Surface topography

This experiment investigated the surface morphologies of silicon oxide films under different substrate temperatures. In practical applications, the $\text{SiO}_x\text{C}_y\text{H}_z$ support layer film has certain surface flatness and compactness requirements. Figure 6 is an SEM image of a sample coated on PET, with a scanning range of $5\ \mu\text{m} \times 5\ \mu\text{m}$. It can be seen that the surface of the film is relatively smooth and dense, the particle size distribution is uniform, and the average particle size is about 110 nm. The actual device fabrication requires the deposition of pyroelectric films on $\text{SiO}_x\text{C}_y\text{H}_z$. Therefore, it is necessary to study the surface condition of $\text{SiO}_x\text{C}_y\text{H}_z$ after high-temperature heat

treatment. Figure 7 is an SEM image of a sample coated on a glass slide, with a scanning range of $10\ \mu\text{m}\times 10\ \mu\text{m}$. It can be seen from the figure that the particle size of the film increases significantly after high-temperature annealing, and the distribution is denser. It can be seen from the figure that the surface of the silicon oxide film is relatively flat, dense, and evenly distributed. With the increase of temperature, scattered larger particles began to appear on the surface of the flat film. This is because the substrate temperature increases the energy of the particles deposited on the substrate surface, the mobility of the particles on the substrate surface increases, and aggregates form clusters or islands.

On the other hand, the high substrate temperature is beneficial for particles to fill the defects on the film's surface, but the higher the temperature is not, the better. From the relationship between the substrate temperature and deposition rate, it can be seen that the higher the temperature, the slower the deposition rate. The decrease of the deposition rate leads to sufficient movement time for the particles on the surface of the substrate, thus forming the morphology of islands and clusters, destroying the denser surface flatness of the film, adversely affecting further micromachining on the film surface. At a reasonable deposition rate, the particles on the substrate surface are covered by subsequent particles before they are entirely aggregated, forming a relatively thick film. However, the faster the deposition rate is not, the better.

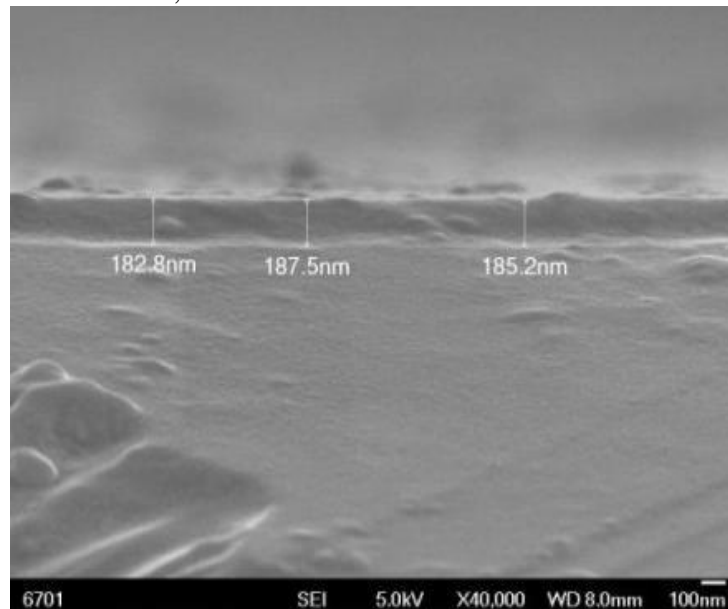


Figure 6: SEM image of a sample coated on PET

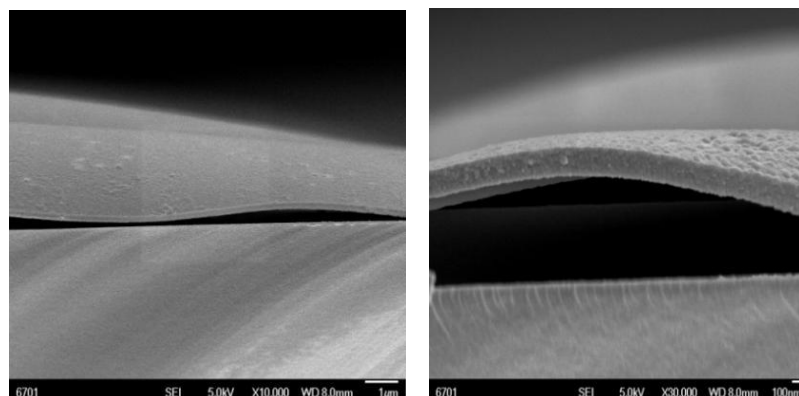


Figure 7: SEM image of a sample coated on a glass slide

It can be seen from the AFM image that the surface morphology of the silicon oxide film prepared by the PECVD method is good (Fig. 8). The surface defectivity can be reduced at an appropriate temperature, and a high-density and flat silicon oxide film can be obtained. However, excessive temperatures or inappropriate deposition rates can affect film quality and yield.

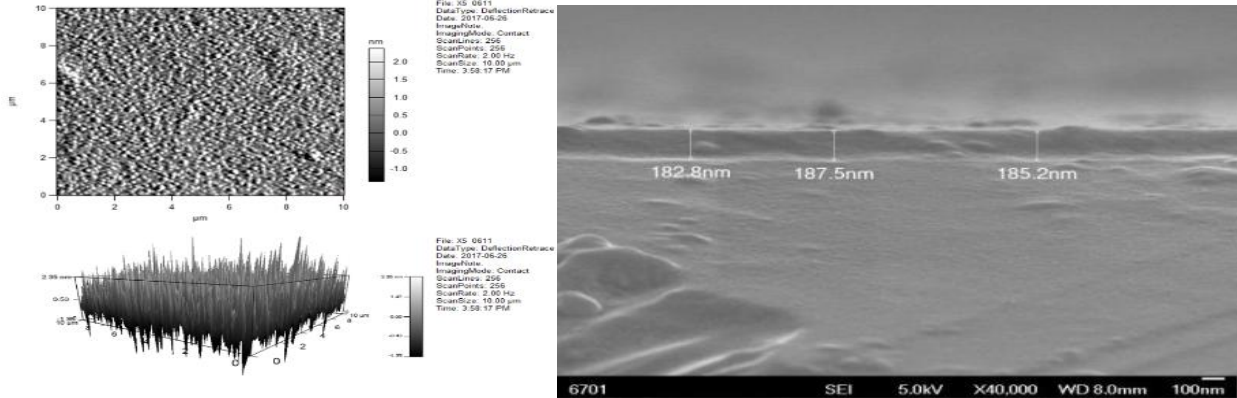


Figure 8: AFM image of the coated sample

4. Conclusion

The silicon oxide film grown by plasma-enhanced chemical vapor deposition has the characteristics of low deposition temperature, fast growth rate, and good uniformity and is widely used in microelectronic mechanical systems. In this paper, based on many experiments, the domestic PECVD equipment is used to deposit silicon oxide films with different stress states, such as high-pressure stress, low-pressure stress, micro stress, low tensile stress, and high tensile stress. Moreover, RF power is described. This has a specific reference value for developing MEMS devices and systems.

Acknowledgments

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