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"Zero" Dependence of Deposition Rate on Deposition Temperature in Photo Chemical Vapor Deposition *

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Abstract　Based on the theoretical analysis and experimental verification, it is presented that there exists a "zero" dependence region in the photo-chemical vapor deposition (photo-CVD) process that the deposition rate does not change with the deposition temperature. The differences reported on the deposition rate with the deposition temperature in photo-CVD are well explained. The result obtained is that between the deposition temperature 100～250℃, under the deposition pressure 200Pa, with the distance between the substrate and the light source being 15～25mm, the deposition rate is basically independent on the deposition temperature change in photo-CVD.

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1　Introduction

Photo chemical vapor deposition is one of the low temperature technologies, without any knock-on damage caused by high-energy ions. It is indicated that SiO_2, Si_3N_4 and SiNO films deposited by the low temperature photo-CVD may not only used as IC mask, isolation and buried layer, but also the ultra-thin gate dielectric of MIS structure devices and the passivation layer of semiconductor devices. The side-wall dielectric of GaAlAs/GaAs HBT can be fabricated with photo-CVD technology, at the same time, low temperature double gaffing with full self-alignment is realized and f_T is raised[1]. For an InSb Infrared detector, protective coating fabricated with photo-CVD improves detection sensitivity and reliability. SiGe/Si heterojunction function materials have been grown by using low temperature photo-CVD[2]. It is reported that the laws of deposition temperature to the deposition rates are different. Some persons think that the deposition rate increases with the rise of

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the deposition temperature (rise law) and others think it decreases with the rise of the deposition temperature (fall law). Why two absolutely contrary laws exist in photo-CVD has not been reported yet. It is considered that there should be a gradual transition zone between "rise law" and "fall law" from photo-CVD technology, with an absolute turning point through "zero" (or called "zero point") in it. In a certain condition, the change of deposition temperature will not affect the deposition rate in some temperature range, which is the so-called "zero" dependence.

2 Experiments

Experiments are conducted based on the Ultra-Violet (UV) CVD technology system which is currently developed by Xidian University. L800T(s) low pressure mercury lamp (made in Japan) acts as the ultraviolet source, which mainly radiates two types of ultra-violet lights with the wavelengths being 185nm and 254nm respectively and the power being 800W. Deep ultra-violet light acts as the excitation source of reaction gases after it transmits the protective gas and the artificial quartz window and then enters into cuboid stainless steel reaction chamber. The semiconductor chip (substrate) is set on the substrate disc in which temperature is controllable and the distance from the substrate disc to the quartz window can be changed. The back ground vacuum of the reaction chamber is obtained from the worm turbo molecular pump and preparative-vacuum pump, and the limiting vacuum is 1×10^{-3}Pa. With SiH_4 and N_2O acting as reaction gases, the SiO_2 film is photolyzed and deposited directly without using photo-sensitizer. Under the conditions of ratio of SiH_4 flow to N_2O/SiH_4 flow keeping constant changing the deposition temperature T (100℃, 150℃, 200℃, 250℃), the deposition pressure P (200Pa, 400Pa, 800Pa), and the distance D from the substrate to the quartz window (4mm, 8mm, 11.5mm, 18.5mm, 46mm), through observing the dependence of the deposition rate on these deposition parameters, we obtain many groups relative experimental curves. Figure1 is a group of typical experimental curves of the dependence of relative deposition rate on a substrate position in the conditions that the deposition temperature keeps 150℃ but the deposition pressures are different. Figure2 is one of the dependence of relative deposition rate on deposition temperatures in case of one deposition pressure 200Pa and different substrate positions.

3 Theoretical analysis and discussion on experimental result

After the reaction gas absorbs ultraviolet light, it continuously produces photo-activation matter. The ones in excitated state will collide freely in the reaction chamber. Therefore, they have a certain average life, and only a part of them can reach the substrate surface through space migration in their life time[4]. They react with the gas molecules absorbed on the substrate surface and make contributions to the deposition film. Supposing that X_s is the space migration length of a photo-activation matter, according to the principle of photo-chemistry and the reaction mechanism of photo-CVD[3] etc., we have derived

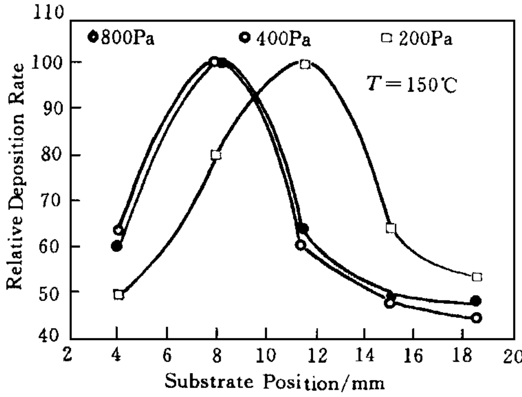

FIG. 1 The dependence of relative deposition rate on the substrate position for photo-CVD SiO_2 film

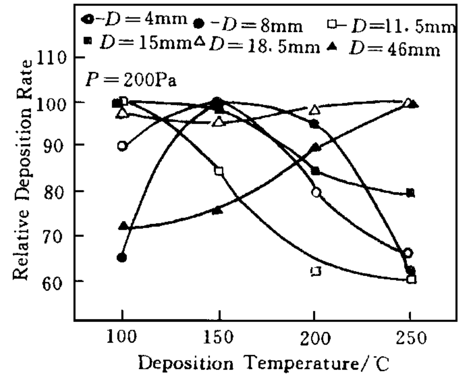

FIG. 2 The dependence of relative deposition rate on deposition temperature for photo-CVD SiO_2 film when substrate position being different

the analytical expression of the total number N of photo-activation matters in cubic deposition reaction space (derivation procedures are neglected) as follows:

$$N = \frac{n_0(\alpha X_s e^{\alpha X_s} - 2e^{\alpha X_s} + X_s + 2)}{2\alpha^2 X_s} \times \frac{D}{e^{\alpha D}}$$

where n_0 is the initial density of the photo-activation species, α is the extinction coefficient, D is the distance from one substrate to a quartz window (may be considered as the distance from one substrate to the light source). It is shown from this expression that the total N of photo-activation matters obeys a rise-maximum-fall law with the increase of distance D, and reaches the peak point at $D = X_s$. The amount of the total number photo-activation matters is actually one characterized deposition rate. The expression reflects the dependence of deposition rate on a substrate position. As shown by the experimental curves in Fig. 1, the relative deposition rate of films with the substrate position follows the above expression, where the maximum relative deposition rate corresponds to D being 8~12mm, which indicates that the space migration length X_s of photo-activation species is different under different deposition pressures. In the cases of D being smaller, obviously $D < X_s$. Due to the distance from the substrate to the quartz window being too short, there is no question that a part of photo-activation matters are intercepted by the quartz window. With D increasing and the interception decreasing, photo-activation matters which contribute to the substrate surface deposition will not continuously increase until $D = X_s$, the maximum value appears. This is the rise part of technology curves. With further increase of D, $D > X_s$. The quantity of photo-activation matters moving to the substrate surface continuously will decrease, and the intensity of light becomes weaker and weaker, the density of photo-activation matters will also drastically decrease, that is, the technology curves display a fall trend. Experimental results shown in Fig. 2 also demonstrate that the deposition rate has a fall trend with the rising of deposition temperatures when D is relative small, and it dose

a rise trend with the rising of deposition temperatures when D is relative large. Figure2 also shows that the deposition rate dose not change with the variation of the deposition temperatures when $D = 18.5$mm, in this way a "zero point" is obtained. Combining the previous analysises, we find that the dependence of deposition rate on deposition temperature follows different laws at different distance from the substrate to the quartz window. When the distance is rather short, the contributory photoactivation matters decrease, and with the rising of deposition temperature, the deabsorptivity of gas moleculeson the substrate surface will also increase, as leads to deposition rate to decrease. When the distance is relative long, the heat activation rate of gas moleculeson the substrate surface will increase, as leads to the deposition rate to rise. So before the "zero point" light excitation plays a dominant role while that "zero point", heat excitation plays a dominant role. In the "zero zone", the contributory photo-activation matters start decrease from the maximum value. With the increasing of deposition temperature, the deabsorptivity of gas moleculeson the substrate surface continuously increases, while the heat activation rate also keeps increasing. So, the light excitation and the heat excitation compensate each other every-where in the different deposition temperature zones, keeping the relative dynamic balance, which makes the deposition rate not change with the variation of deposition temperatures, as shown as a "zero" dependence. It should be point out that a "zero point" zone is the transition zone of light excitation to heat excitation, but not the zone in which deposition rate is maximum, which also verified by the experimental results. For our technology system, when deposition pressure is 200Pa, "zero point" is between the 15~25mm distance range from the substrate to the light source (quartz windows).

With "zero" dependence suggested by us, satisfactoly explaination one obtained about the two contrary points between deposition rate and deposition temperature in photo-CVD. Considering practical applications, with the zero dependence either designing technology system or conducting film growth, can neglect the importance of the accuracy of controlling the temperature of the substrate, the uniform distribution of the temperature of large size substrate etc., and we may obtain very good film deposition uniformity and repeatability easily. The results reported in the paper have been verified with the experiments of photo-CVD-SiO_2 film, and they are also suitable for the deposition or growing other film materials using photo-CVD technology.

4 Conclusions

Based on the mechanism of photo-CVD reaction, combined light excitation with heat excitation theories, and with the concept of space migration length of photo-activation matters, we have derived an analytical expression of sum total number photo-activation matters in a cubic reaction region, and theoretically obtained the rise-maximum-fall law on the sum total photo-activation matters varying with the distance from the substrate to the light source. When the distance equals to the space migration length of photo-activation

matters, the maximum point appears, at this time the deposition rate being maximum. The distance corresponding to maximum deposition rate obtained through experiments is 8～12mm. Because the generating light excitation is accompanied by heat excitation, there is the "zero" dependence of deposition rate on deposition temperature in the transition zone of light excitation and heat excitation, that is, in the range of lower temperature, for our technology system, when the distance from the substrate to the light source is 15～25mm, under the condition of deposition pressure being 200Pa, deposition rate is basically not affected by the change of the deposition temperatures

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