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ORIGINAL RESEARCH ARTICLE

Study on properties of silicon nitride film prepared by PECVD for solar cells

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ABSTRACT

Silicon nitride film containing hydrogen is widely used as antireflection layer and passivation layer in the field of solar cell industrial production. Silicon nitride films containing hydrogen were prepared by industrial plasma enhanced chemical vapor deposition (PECVD) equipment. Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the composition of the film, to study the influence of reaction gas flow rate and high-frequency power on the composition and properties of the film, and to study the influence of silicon nitride film composition on the passivation effect of the silicon wafer through the minority carrier life of the silicon wafer, so as to clarify the direction of process adjustment in actual industrial production.

Keywords: PECVD; Fourier Transform Infrared; Silicon Nitride Film; Passivation

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1. Introduction

With the increasing shortage of energy and the increasing urgency of environmental protection, renewable green energy has attracted more and more attention. Silicon solar cell is one of the research hotspots and occupies a dominant position in market application. In order to maximize the use of sunlight, a layer of silicon nitride film will be deposited on the surface of silicon solar cells as antireflection film. Silicon nitride film has good insulation, compactness, stability and masking ability to impurity particles, which can significantly improve the conversion efficiency of the battery, but its characteristics largely depend on the preparation conditions of the film[1–3]. In recent years, plasma enhanced chemical vapor deposition (PECVD) is widely used to prepare silicon nitride films in industry and laboratory.

In PECVD process, the reaction power comes from electrons and ions accelerated by high-frequency electric field. They collide with reaction gas molecules and ionize gas molecules into various active groups. The ionization of reaction gas will directly affect the composition and properties of silicon nitride films. The characteristics of silicon nitride films have been widely studied in the laboratory, but there are few studies based on the industrial production of solar cells. In this paper, silicon nitride films are prepared on silicon wafers by industrial PECVD, the relationship between PECVD process parameters and film composition in industrial production is studied, and the influence of high temperature and rapid heat treatment process on film composition is analyzed. By comparing the passivation property of silicon nitride films prepared by different process parameters, the influence of film characteristics on the conversion efficiency of solar cells is finally clarified.

2. Growth mechanism of silicon nitride films prepared by PECVD

In non-equilibrium plasma, the temperature of molecules, atoms, ions or activating groups is the same as the ambient temperature, while the average temperature of non-equilibrium electrons can be 1–2 orders of magnitude higher than that of other ions under the action of high-frequency electric field due to their small mass. The preparation of silicon nitride thin films by PECVD method uses this characteristic to dissociate and activate the reaction gas in the reaction chamber under the action of high-temperature electrons, and adsorb it on the substrate surface for chemical reaction, so as to prepare new dielectric thin films at low temperature. The formation process of silicon nitride film can be divided into the following steps[4]:

2.1 Gas dissociation

Ammonia enters the cavity and is dissociated by high-temperature electrons. The chemical reaction is as following:

$$NH_3 + e^- \rightarrow NH_b + H_{(3-b)} + e^- \tag{1}$$

Silane enters the cavity and is dissociated by high-temperature electrons. The chemical reaction is as following:

$$SiH_4 + e^- \rightarrow SiH_a + H_{(4-a)} + e^- \tag{2}$$

The types of dissociation products of ammonia and silane are directly related to process parameters such as gas flow and high-frequency power.

2.2 Ammonia and silane molecular fragments are combined again to form new molecules

The components in the plasma are very complex and always in the process of dynamic equilibrium. Among them, a kind of molecule that plays a key role in the growth of silicon nitride film is called aminosilane[5,6]. Aminosilane is connected by Si–H bond and N–H bond in the plasma to form Si–N bond.

$$SiH_a + NH_b \rightarrow SiH_{(a-c)}(NH_{b-1})_c + H \tag{3}$$

Aminosilane is a kind of molecular assembly, and its specific composition is determined by the composition in the plasma.

2.3 Bonding between groups to form a skeleton

Aminosilane molecules are adsorbed on the surface of silicon wafer. Under the action of silicon wafer temperature, the Si–H bond between molecules reacts with N–H to form Si–N bond.

$$Si{-}H + H{-}N \rightarrow Si{-}N + H \tag{4}$$

The connection between silane fragments and ammonia fragments in plasma is completed by the reaction between Si–H and N–H[7]. With Si–N bond as skeleton, adjacent molecules are continuously connected, and gradually epitaxial silicon nitride film structure is formed. In the process of skeleton formation, the free molecules in the plasma are connected to the skeleton through the reaction between Si–H bond and H–N bond. The ratio of various groups in plasma gas directly determines the structure of $Si_xN_yH_z$ film and has a direct impact on the properties of the film.

The ionization of gas plays a decisive role in the composition of silicon nitride film. In silane, the bond energy of Si–H is 3.2 eV, and in ammonia, the bond energy of N–H is 4.2 eV. Under the action of high-frequency power supply, the ionization of silane in the mixed gas is prior to that of ammonia. Only when the silane is fully ionized and the high-frequency power supply is continuously increased, the ammonia will be fully ionized. If the highfrequency power is low and the silane ionization is insufficient, the free silane molecules in the plasma will react with aminosilane molecules to form ethylaminosilane[4,5].

$$SiH_4 + SiH_{a-c}(NH_b)_c \rightarrow Si_2H_{a-c}(NH_b)_{c-1}(NH_{b-1}) + H \tag{5}$$

Ethylaminosilane can also form a skeleton and grow epitaxially into silicon nitride film. The silicon nitride film grown from ethylaminosilane has low mass density and poor passivation effect[8]. The passivation effect of silicon nitride film on silicon wafer comes from the H atom released during sintering. Si–H bond breaks at about 600 °C and N–H bond breaks at about 800 °C. Both reactions will release H atoms, but in silicon nitride films with low mass density, H atoms can easily combine with each other to form molecules. In silicon nitride films with high mass density, H atoms have sufficient time to migrate into silicon wafers[8,9]. H atom has a good passivation effect on the surface and internal defects of silicon wafer, and hydrogen molecule has no passivation effect on silicon wafer.

3. Experimental process

Silicon nitride thin films were prepared by PECVD equipment of the 48th Research Institute of China Electronics Technology Group Corporation, and the frequency of highfrequency signal generator was 40 kHz. The gases used are high-purity ammonia and high-purity silane. During the experiment, the reaction gas is directly introduced into the reaction chamber. The pressure of the reaction chamber is 200 Pa, the reaction temperature is 400 °C, the ammonia flow is 5,000 sccm, the silane flow range is 300–1,200 sccm, and the power range of high-frequency power supply is 5–8 kW. The composition of the film was analyzed by Nicolet 6,700 Fourier transform infrared spectroscopy of Thermo Fisher Scientific. CDF type high-temperature sintering furnace produced by Despatch is used for high-temperature rapid heat treatment of silicon nitride film, and WCT120 minority carrier life tester of Sinton company is used for minority carrier life test.

4. Experimental results and discussion

4.1 Effect of high-frequency power on refractive index and growth rate of silicon nitride film

Silicon nitride films were prepared under different power conditions. The high-frequency power was 3–8 kW, the silane flow rate was 900 sccm, the ammonia flow rate was 5,000 sccm, the reaction chamber pressure was 200 Pa and the reaction temperature was 400 °C. Twelve silicon wafers were extracted from each condition, and 5 points of data were tested for each wafer, and the average value was taken.

With the increase of high-frequency power, the refractive index of the film shows a curve change. The refractive index of silicon nitride film is determined by the silicon nitrogen ratio in the film, and the silicon nitrogen ratio of the film is determined by the ratio of silicon atom group and nitrogen atom group in the plasma. When the mixed gas of silane and ammonia is affected by high-frequency power supply, the ionization of silane and ammonia will be different, and the difference of ionization will lead to the change of refractive index and growth rate[7].

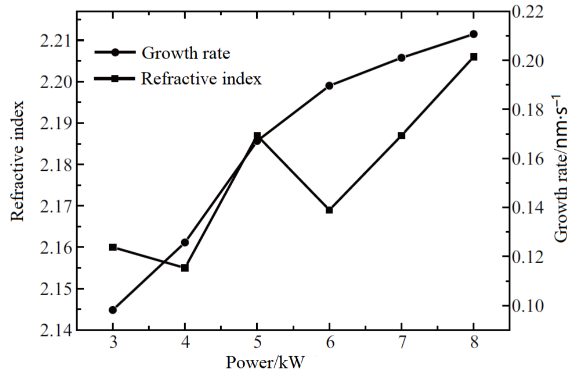

Figure 1. Refractive index and growth rate of silicon nitride films prepared at different powers.

When the power increases from 3 kW to 8 kW, the refractive index shows a decreasing – increasing – decreasing – increasing curve. The growth rate of the film increases with the increase of high-frequency power. It increases rapidly in the range of power 3–5 kW and slowly in the range of power 6–8 kW.

4.2 Effect of high-frequency power on refractive index and thickness uniformity of silicon nitride film

With the increase of high-frequency power from 3 kW to 8 kW, the standard deviation of refractive index shows a trend of The standard variance of refractive index shows a trend of first decreasing – slowly rising – decreasing – rapidly rising. The standard variance of film thickness showed a decreasing – rising – decreasing trend with the increase of high-frequency power from 3 kW to 8 kW.

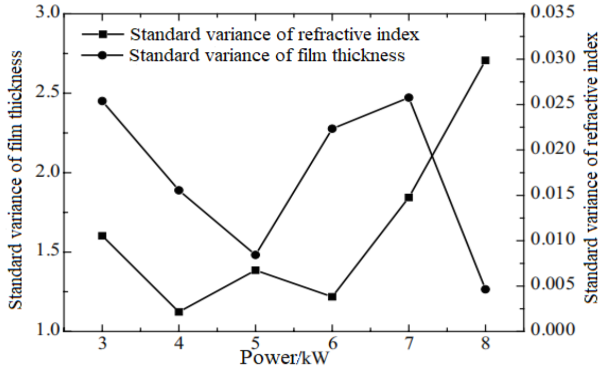

Figure 2. Standard deviation relationship between refractive index and film thickness of silicon nitride films prepared by different power.

4.3 Effect of silane flow rate on refractive index and growth rate of silicon nitride film

Silicon nitride films were prepared under different silane flow rates. The silane flow rate ranged from 400 to 1,200 sccm, the high frequency power was 5 kW, the ammonia flow rate was 5,000 sccm, the reaction chamber pressure was 200 Pa and the reaction temperature was 400 °C. Twelve silicon wafers were extracted from each condition, and 5 points of data were tested for each wafer, and the average value was taken.

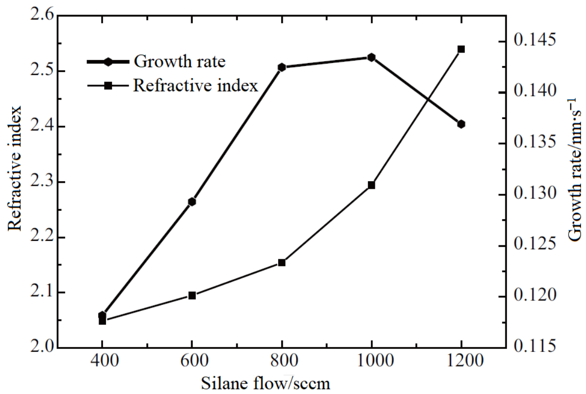

Figure 3. Relationship between refractive index and growth rate of silicon nitride films prepared by different silane flow rates.

The refractive index of the film increases rapidly, when the silane flow rate is from 400 to 800 sccm. The growth rate of the film increased rapidly – increased slowly – decreased rapidly. The growth rate of silicon nitride film is directly related to the density of aminosilane in the plasma, which shows that when the silane flow reaches a certain degree, the density of aminosilane in the plasma will decrease.

4.4 Effect of silane flow rate on refractive index and thickness uniformity of silicon nitride film

With the increase of silane flow rate, the standard deviation of film thickness and refractive index decreased first and then increased. When the silane flow rate is 800 sccm, the standard deviation of film thickness and refractive index reaches the lowest value at the same time.

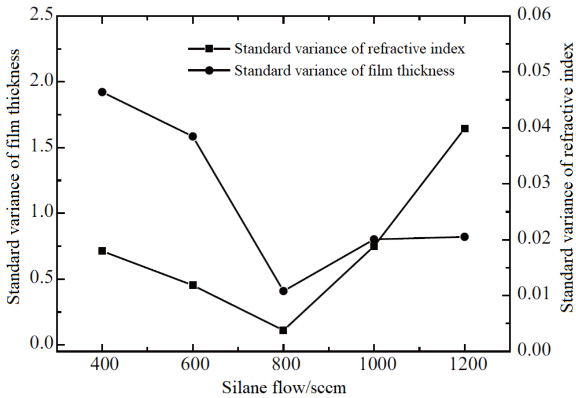

Figure 4. Relationship between refractive index and standard deviation of film thickness of silicon nitride films prepared by different silane flow rates.

4.5 Effect of high-frequency power on composition of silicon nitride film

The Fourier transform infrared spectroscopy of silicon nitride films prepared under different power conditions were measured. The power range was 3–8 kW, the silane flow rate was 900 sccm, the ammonia flow rate was 5,000 sccm, and the pressure of reaction chamber is 200 Pa and the reaction temperature is 400 °C.

It can be seen from **Figure 5** that when the high-frequency power is 3 kW, the N–H and N–H_2 absorption peaks cannot be observed. With the increase of high-frequency power, the N–H and N–H_2 bond absorption peaks in the spectral curve gradually strengthen. This is because when the power is 3 kW, the dissociation rate of NH_3 molecules is low[7]. The number of nitrogen molecules in the plasma is relatively small, all activated nitrogen molecules are involved in the formation of aminosilane, and there are no free nitrogen molecules in the plasma, so there are no N–H and N–H_2 groups in the silicon nitride film. With the increase of high-frequency power, the number of activated nitrogen molecules in the plasma increases, and the free nitrogen molecules begin to connect directly to the skeleton of silicon nitride film.

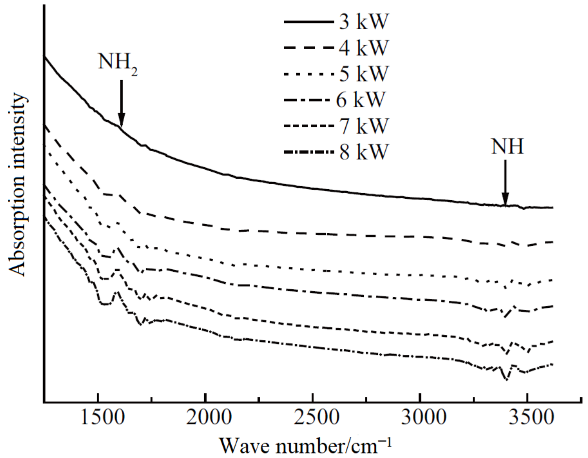

Figure 5. Infrared spectra of silicon nitride films prepared at different powers.

4.6 Effect of silane flow rate on composition of silicon nitride film

The FTIR spectra of silicon nitride films prepared under different silane flow rates were measured. The silane flow rate range was 400–1,200 sccm, the ammonia flow rate was 5,000 sccm, the high frequency power was 5 kW, the reaction chamber pressure was 200 Pa and the reaction temperature was 400 °C.

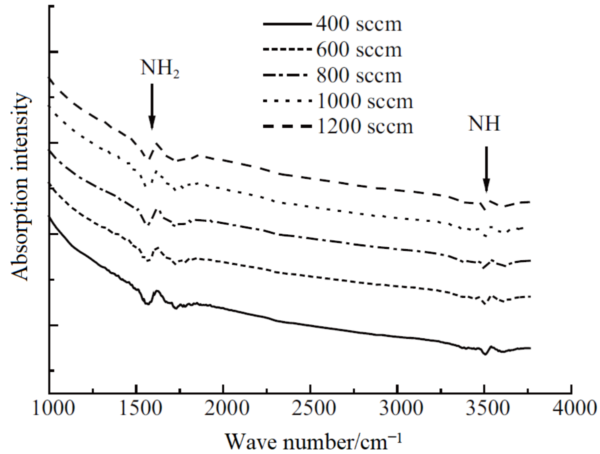

Figure 6. Infrared spectra of silicon nitride films prepared under different silane flow rates.

N–H and N–H_2 absorption peaks were observed in all spectral curves. Silane flow rate had little effect on N–H and N–H_2 groups in silicon nitride films.

4.7 Influence of film composition on passivation effect and corrosion rate

In order to determine the passivation effect of silicon nitride film on silicon wafer, the minority carrier lifetime of silicon wafer was measured before and after coating. The minority carrier lifetime of silicon wafer after rapid heat treatment is measured to measure the effect of rapid heat treatment on the passivation of silicon nitride film. The rapid heat treatment process adopts the standard battery sintering process, and the silicon wafer is coated on both sides. The results are shown in **Table 1**.

The passivation effect of silicon nitride film

Table 1. Minority carrier lifetime test diagram of silicon wafer before coating, after coating and after rapid heat treatment

Sample	Silane flow rate /sccm	Ammonia flow rate/ sccm	High-frequency power /kHz	Minority carrier lifetime /µm	Minority carrier lifetime (after annealing) /µm
a	900	5,000	3,000	35	56
b	900	5,000	8,000	47	106
c	400	5,000	5,000	52	102
d	1,200	5,000	5,000	46	108

on silicon wafer comes from the H atom produced during deposition[9], the H atom in plasma comes from the dissociation of gas, and the frequency power directly affects the dissociation rate of gas. Because of the lowest high frequency power, sample a is of the lowest minority carrier lifetime. The passivation during rapid heat treatment comes from the H atom formed by the fracture of N–H bond in silicon nitride. According to the test results of Fourier transform infrared spectroscopy, the number of N–H and N–H_2 groups in sample a are the least, so the minority carrier lifetime increase of sample a is the lowest, and the number of N–H and N–H_2 groups in samples b, c and d are the same, so the difference of minority carrier lifetime increase is small.

4.8 Effect of silicon nitride film on conversion efficiency of solar cells

In order to ensure good antireflection effect, the optical thickness of silicon nitride is controlled at about 160 nm. Due to the characteristics of single-crystal suede, the incident light will be reflected on the silicon wafer surface for many times and pass through the silicon nitride film for many times. Therefore, on the single-crystal solar cell, the light absorption coefficient of silicon nitride has a significant impact on the cell efficiency, and the light absorption coefficient of silicon nitride increases with the increase of refractive index[10]. Under the influence of minority carrier lifetime and refractive index, the conversion efficiency of sample c is the highest and that of sample d is the lowest.

Table 2. Effect of PE parameters on battery efficiency

Sample	Silane flow rate / sccm	Ammonia flow rate/sccm	High-frequency power /W	Film thickness / nm	Refractive index *n*	Battery efficiency /%
a	900	5,000	3,000	75.1	2.16	19.72
b	900	5,000	8,000	73.4	2.20	19.84
c	400	5,000	5,000	78.1	2.06	19.98
d	1,200	5,000	5,000	67.7	2.41	19.67

5. Conclusion

The refractive index and growth rate of thin films are determined by gas flow and high-frequency power supply. By adjusting the gas flow and high-frequency power matching, the standard deviation of refractive index and film thickness can be minimized, i.e., there is an optimization condition to optimize the consistency and uniformity of silicon nitride film.

The ionization degree of reaction gas and the composition of silicon nitride film are directly determined by the reaction gas flow and high-frequency power supply.

The composition of silicon nitride film directly determines the passivation effect of silicon nitride film. Before and after rapid heat treatment, the passivation effect of films with high content of N–H and N–H_2 is obviously strengthened, but the cell efficiency is affected by both the passivation effect and the extinction coefficient of films.

Conflict of interest

The authors declare that they have no conflict of interest.

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