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Characterization of As-deposited and Annealing SiN Films Deposited by Plasma Enhanced Chemical Vapour Deposition*

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Abstract: Silicon nitride (SiN) thin films were deposited by PECVD (Plasma Enhanced Chemical Vapour Deposition) of silane (SiH_4) and ammonia (NH_3) reactants. Subsequently they were annealed in a furnace or rapid thermal processing (RTP) on different conditions (temperature, time and ambient). SiN thin films are used not only as very efficient antireflection coating but also as surface and bulk passivation on silicon solar cells. The characterization of SiN thin films was studied by spectral ellipsometry, reflection spectra, infrared absorption spectroscopy (IR) and quasi-steady state photoconductance (QSSPC) measurements. It was found by means of spectral ellipsometry that the thickness of SiN films decreased and the refractive index increased as the annealing temperature increased, which were most likely due to the more and more compact structure of SiN films. The reflection index was also investigated. There was significant hydrogen incorporation as well as the characteristic Si-N bands in the IR spectra. The hydrogen content in SiN thin films can be determined followed by integration of Si-H and N-H absorption bands. The effective minority carrier lifetimes of the samples were measured by QSSPC. The efficiency of SiN passivation was related with hydrogen content.

Key words: silicon nitride; PECVD; annealing
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1 Introduction

Silicon nitride thin film is a kind of very important material with excellent photoelectric properties, stability, passivation and mechanical properties. It has a wide application prospect in the fields of microelectronics, photoelectrons and surface modification of materials. There has been a great interest in applications of silicon nitride films deposited by PECVD (Plasma Enhanced Chemical Vapor Deposition) on silicon solar cells, SiN films not only reduce optical losses but also simultaneously provide an outstanding degree of surface and bulk passivation. As antireflection coating, the index of refraction of SiN films is approximate 2.0, which is most suitable in all medium films ever used on solar cells. Moreover, hydrogen passivation via PECVD SiN films is very efficient, especially for multi-crystalline solar cells[1-3]. After low temperature deposition of SiN films, surface recombination velocity (SRV) decreases greatly to 20 cm/s[4], even superior to thermal silicon oxide.

There are a few high temperature processes during solar cells fabrication, such as sintering of the contacts. High temperature treatment may charge characterization of SiN films. In this paper, characterization of as-deposited and annealing on different conditions silicon nitride films is investigated.

2 Experimental

The substrates were 700 μm thick, polished 10 Ω·cm *p*-type CZ silicon wafers with a (100) surface orientation. Silicon nitride thin films were symmetrically deposited at low temperature (< 400 ℃) by PECVD onto both surfaces of the RCA-cleaned wafers. The reactant gases were ammonia and a silane/nitrogen mixture (2.5% silane, 97.5% nitrogen). The silane/nitrogen mixture was much safer than pure silane gas as it was not flammable in direct contact with air. Subsequently some of them were annealed in a furnace or rapid thermal processing (RTP) on different conditions (temperature, time and ambient). The characterization of SiN films was measured respectively by means of spectral ellipsometry, reflection spectra, infrared absorption spectroscopy (IR) and quasi-steady state photoconductance (QSSPC) measurements.

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3 Results and discussion

3.1 Antireflection coating

The thickness and refractive index of SiN thin films were measured by spectral ellipsometry. Fig. 1 is the comparison of the thickness and refractive index of SiN films after different temperature annealing for one hour in N_2 atmosphere. With annealing temperature was increasing, the thickness of SiN films was decreasing and refractive index was increasing. This indicated SiN thin films were more and more compact as annealing temperature was increasing.

The index of reflection is very important for antireflection coating. The result of measurement showed the reflection index was not greatly various because the thickness and refractive index both changed.

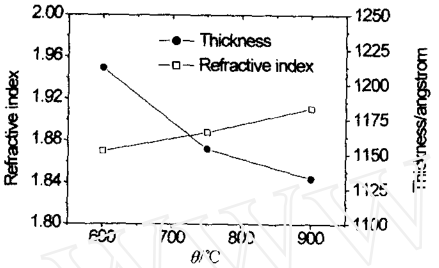

Fig. 1 Characteristics of SiN films after annealing

3.2 SiN passivation

The IR equipment 670FT model (Nicolet Company) was used to measure the IR absorption spectra of all SiN thin films including as-deposited and annealing samples at different conditions.

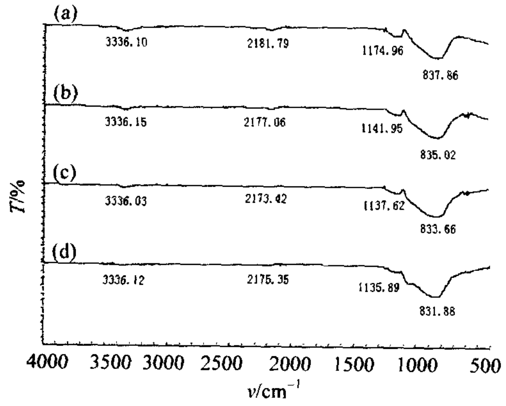

Fig.2 IR absorption spectra for SiN films

(a) as-deposited; (b) 600 ℃ annealing,

(c) 750 ℃ annealing, (d) 900 ℃ annealing

Fig.2 displays IR spectra of (a) as-deposited and (b) - (d) annealing SiN thin films at different temperatures (600 ℃, 750 ℃, and 900 ℃) for one hour in N_2 atmosphere. From Fig. 2 (a), it shows significant hydrogen incorporation as well as the characteristic Si-N features. A strong Si-N stretching vibration mode is at 830 cm^{-1}, and the additional weaker absorption peaks at 3330 cm^{-1}, 2160 cm^{-1}, 1170 cm^{-1} are all associated with bonded hydrogen. The spectra show N - H stretching and bending vibration modes at frequencies of 3330 and 1170 cm^{-1}, respectively, and show Si-H stretching vibration mode at 2160 cm^{-1}[5,6].

According to the method of W.A. Lanford and M.J. Rand, hydrogen content of these films can be determined by means of N-H and Si-H absorbance peaks[5]. In the as-deposited SiN thin films, hydrogen content was 1.6×10^{18} cm^{-2}. After annealing at 600 ℃, for one hour, hydrogen content decreased to 1.06×10^{18} cm^{-2}, and after annealing at 750 ℃, it was 5.6×10^{17} cm^{-2}. That was to say, 2/3 of hydrogen had been released from the samples. Fig.2(d) shows the N-H and Si-H absorbance peaks are too weak to calculate hydrogen concentration after annealing at 900 ℃.

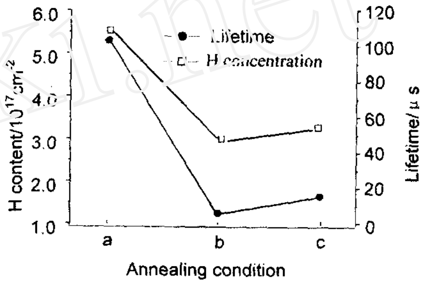

Fig.3 Hydrogen content and minority carrier lifetimes of SiN films

(a) as-deposited; (b) 850 ℃ 30 s RTP annealing;

(c) 830 ℃ 30 min furnace annealing

Fig. 3 shows the bonded hydrogen content and effective minority carrier lifetimes of the samples of (a) as-deposited, (b) RTP annealing at 850 ℃ for 30 s in N_2 atmosphere and (c) furnace annealing at 830 ℃ for 30 min in N_2 atmosphere. As can be seen from Fig.3, the minority carrier lifetimes of the wafers with as-deposited SiN films reached 105.6 μs which was much higher than 10 μs that was the lifetime of the substrates without SiN films. After high temperature annealing, the effective minority carrier lifetimes both decreased severely without reference to the different of annealing methods. Meanwhile, hydrogen content of SiN thin films also quite decreased after the two method annealing.

Fig.4 shows IR absorption spectra of SiN thin films after furnace annealing at 900 ℃ for 10 min (a) in N_2 atmosphere and (b) in H_2 atmosphere. A new Si-O-Si stretching vibration mode at 1110 cm^{-1} is found, indicating considerable oxygen existence. By means of N-H and Si-H absorbance peaks, hydrogen content was 0.47×10^{17} cm^{-2} (N_2) and 1.21×10^{17} cm^{-2} (H_2), respectively. At the same time, the effective minority carrier lifetimes of the samples also were measured. It was 5.7 μs after annealing in N_2 atmosphere and 45.1 μs in H_2 atmosphere. Compared with the lifetime 47.0 μs of the samples without annealing, the lifetime decreased prominently after N_2 annealing but did not change considerably after H_2 annealing.

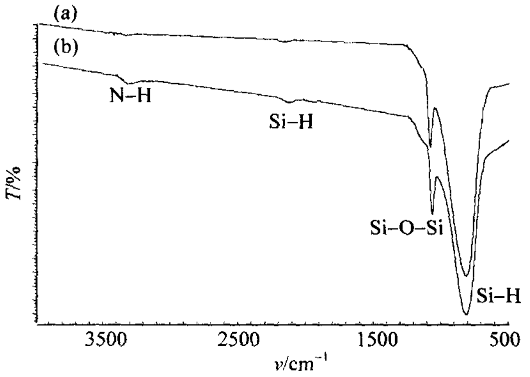

Fig.4 IR absorption spectra
(a) N_2 atmosphere; (b) H_2 atmosphere

Consequently, the efficiency of SiN passivation had relations with hydrogen content. SiN films fabricated with the high-frequency direct PECVD can provide significantly superior surface passivation[7]. After annealing, part of hydrogen effused from SiN thin films and diffused into the bulk of Si wafers so as to get an effective hydrogen passivation of bulk defects. But if annealing temperatures were excessively high, hydrogen in Si wafers also effused so as to hydrogen content decreased greatly and the effect of bulk passivation extincted. So optimized annealing conditions were important for the silicon solar cells with SiN films.

4 Conclusions

Different annealing conditions had a great effect on characterization of SiN thin films. The thickness of SiN films decreased and the refractive index increased with the annealing temperature increased. This indicated SiN thin films were more and more compact as annealing temperature was increasing. There was considerable hydrogen content in SiN thin films by IR spectra. The effective minority carrier lifetimes of the samples improved greatly after deposition of SiN films. The efficiency of SiN passivation was related with hydrogen content. After annealing in H_2 atmosphere, lifetime did not decrease prominently. After high temperature annealing in N_2 atmosphere, most of hydrogen effused from SiN thin films and the effect of passivation extincted.

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PECVD 氮化硅薄膜的沉积和退火特性

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摘　要：利用等离子增强化学气相沉积（PECVD）方法沉积了氮化硅薄膜，反应气体为氨气和硅烷。这些薄膜在不同条件（温度、时间和气氛）下进行了炉温或快速退火。对太阳电池而言，氮化硅薄膜不仅是有效的减反射层而且也有表面钝化和体钝化作用。利用椭圆偏振光谱、反射谱、红外吸收谱和准稳态光电导（QSSPC）分析了氮化硅薄膜的特性。实验发现随着退火温度的增加，氮化硅薄膜的厚度下降而折射率增加，可以归因于在退火过程中，薄膜愈加致密。红外吸收谱的研究发现，氮化硅中氢的含量在退火过程中有明显的下降，而 QSSPC 测量的样品寿命有同样的变化。这些结果显示氮化硅的钝化作用与其中的氢含量有关。

关键词：氮化硅；PECVD；退火
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