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Investigation of surface passivation by dual layers SiN_x/SiO_2 coating on CZ silicon wafer

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Abstract: Recombination centers are a significant loss mechanism in solar cells. To achieve high efficiency, recombination losses should be minimized. The surface passivation technique is used to minimize recombination losses, therefore to achieve high conversion efficiency, especially for crystalline Silicon (c-Si). In this study, we have investigated the passivation properties of the silicon surface by combined double stack layer SINx-H/SiO_2; the characteristics of the deposited films are strongly dependent on surface preparation, deposition process, annealing parameters, etc. Thereby, Fourier Transformed Infrared spectroscopy FTIR was used to analyze the chemical composition of the double stack SiNx/SiO_2, and the effective lifetime is used to evaluate the minority carrier lifetime (τ_{eff}) by means of Quasi Steady State Photo-Conductance (QSSPC), the τ_{eff} remains rather weak after the deposition of the double layer SiNx / SiO_2 because of the appearance of an inversion layer inducing a switching of the type of semiconductor. Annealing at 400°C under a pressure of 25 milliTorr allowed an improvement in effective lifetime of minority carriers leading to an enhancement in the surface passivation related to the reduction of paramagnetique defects and the improvement in the statistical distribution of different bonding environments deduced from the calculation of the full width at half maximum FWHM of the Si–O stretching , so that a lower value of the FWHM means a lower dispersion of local environments and a higher structural order of the film.

Keywords: *Passivation, SiNx/SiO_2, FTIR, QSSPC.*

1. INTRODUCTION

Silicon oxide (SiO_2) and silicon nitride (SiNx :H) are the most extensively used dielectrics in the microelectronics industry. In photovoltaic applications we used these two dielectrics as a double stack SiNx/SiO_2 for the passivation of the silicon surface. The Si/SiO_2 system is characterized by excellent interface and electrical properties. But despite these advantages, the thermal oxidation has not been implemented into the majority of industrial cell processes up to now because of the high sensitivity of the silicon bulk lifetime to high-temperature processes [1], the thin films of SiO_2 are also sensitive to tunneling currents and permeability to boron and alkali ion diffusion, adding to this the formation of boron-iron (FeB) pairs under the effect of oxidation temperature [2].
SiN*x: H* shows better impermeability properties than SiO_2, as well as a higher dielectric constant which allows physically thicker dielectrics with the same capacitance–voltage performance [3]. Different approaches have been developed to combine the properties of SiO_2 and SiN*x: H*, such as stacked oxide–nitride structures [4].

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In this study, we have investigated the passivation behavior of the silicon surface by the double stack SINx-H/SiO_2.
Fourier Transform Infrared Spectroscopy (FTIR) was employed in the absorbance mode with the correction of the baselines in order to characterize the bonding and structural properties of the films. This technique provides information on the different bonds present in the film, as well as information regarding the structural order, since the width of these bands is related to the different bonding environments [5]. In order to evaluate the quality of passivated Si wafer, effective carrier lifetime was measured using quasi-steady state photoconductance (QSSPC). Additional characterizations of optical characteristics and interface defects have also been undertaken within this work.

2. EXPERIMENTAL

Boron-doped <100> oriented Cz- Silicon wafers of 320 µm thickness and 1–3 Ω cm resistivity with 10 µs of minority carrier lifetime were used in this study. The silicon wafers were cleaned following the piranha etches procedure before oxidation process.
A conventional thermal oxide (CTO) with a thickness of 10 nm was achieved in a quartz tube furnace using the N_2/O_2 gas flow at 950°C. Then, SiNx film was deposited on the Oxidized samples using Plasma-enhanced chemical vapor deposition (PECVD) techniques with ultra-high purity SiH_4 and NH_3 precursor gases. Each wafer was cut into two parts, as-deposited, which are nonannealed samples and annealed samples; these later have been annealed in tube furnace 400°C at low pressure. Once this step was achieved, we measured the minority carrier lifetime using the QSSPC instrument, for both groups of samples. The QSSPC measurements showed an enhancement in minority carrier lifetime after a low pressure thermal annealed. FTIR characterizations were done in the 400– 4000 cm^{-1} range with a Thermo Nicolet FTIR spectrometer in order to characterize the bonding and structural properties of the films. In this work, we further investigate the optical characteristics of the film by means of UV–visible-NIR optical reflectivity spectrophotometer (Carry 500 Varian), and the hot probe method (surface conductivity type) in order to investigate whether there is an apparition of an inversion layer at the surface of the samples after oxidation process.

3. RESULTS AND DISCUSSION

3.1. QSSPC characterization

The effective lifetime (τ_{eff}), here the term "effective" minority carrier lifetime (hereafter minority carrier lifetime or τ_{eff}) includes both surface and bulk components. The QSSPC results for the samples passivated with SiNx/SiO_2/p-Si are shown in figure 1. As can be seen from this figure, the CTO layers achieved a low degree of passivation on p type c-Si, τ_{eff} = 3.96 µs. More improvement lifetimes are obtained by SiNx/SiO_2 stacks (τ_{eff} = 13,29 µs), this improvement is due to the hydrogen supply of the SiNx-H layer. The annealing at 400°C in N_2 ambient under 25 milliTorr improved minority carrier lifetime of the samples passivated with SiNx/CTO schemes, it seems clear that SiNx/CTO after annealing gives a better surface passivation quality on the low-resistivity (1-3 Ω.cm) p-Si.

This significant improvement of lifetimes before and after annealing can be ascribed to the reducing of the surface states density, via SiNx/SiO_2 passivation. As a result of the SRH (Shockley-Read-Hall) theory [6], the τ_{eff} is largely depends on the surface states (defects and dangling bonds).

In order to improve the understanding of the related mechanisms causing to the lifetime enhancement after annealing process, we conducted an infrared spectroscopy (FTIR) investigation.

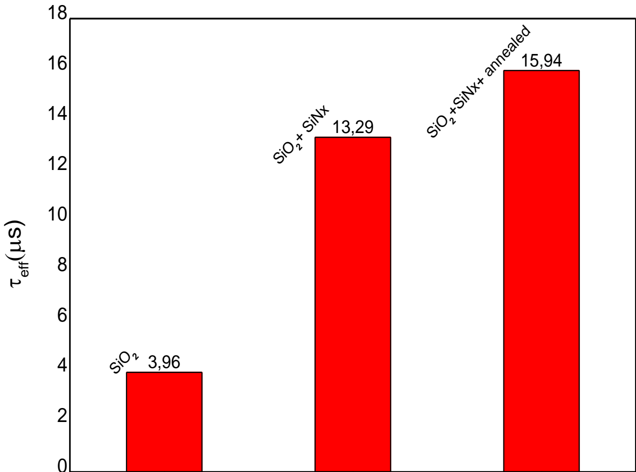

Fig.1. Effective minority lifetime of different passivation scheme on a 1-3 Ω.cm p-type Cz silicon wafer

3.2. FTIR investigation

The FTIR absorbance spectra of the samples with the SiNx/CTO stacks are shown in Fig. 2.

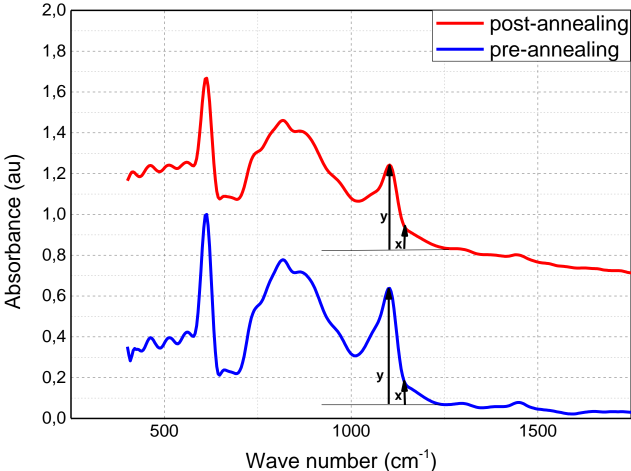

Fig.2. FTIR absorbance spectra of SiNx/SiO_2(thermal) stacks before and after annealing process at 400°C

The main absorption band for SiO_2 connected with stretching vibrations of bridging oxygen atoms is known to be within the wavenumber range 1000–1100 cm^{-1}, and the position of the peak depends on the structural arrangement of the oxygen atoms [7, 8].
As it can be seen from figure 2, the characteristic bands almost at 1100 cm^{-1}, 462 cm^{-1} and 818 cm^{-1} are corresponding to the Si-O stretching, bending and rocking respectively [9]. Plasma-deposited silicon nitride films are characterized by the presence of significant amounts of H in the form of N–H, Si–H and the most prominent feature on the spectrum of silicon nitride film is the peak due to Si–N bonds [10]. The peak located at (1290 - 1300 cm^{-1}) can be attributed to the N–H wagging mode, because this peak disappears after annealing at 400°C; it is well known that the weaker N–H bonds break up more easily than the more stable Si–H bonds during annealing, knowing that the desorption of hydrogen start at 400°C as reported by j. F Lellievre [11]. The hydrogen set free from the N–H bonds passivates silicon dangling bonds within the bulk [12, 13]; this can be the first reason to explain the enhancement of τ_{eff} after annealing. Moreover, the peak at 613 cm^{-1} is related to Si-Si stretching mode [14]. The features at around 865 cm^{-1} peak are related to Si-N stretching bond [10]. No Si–H bonds were detected, which is expected due to the high N/Si ratio [12]. Once more, the FTIR spectra shows a peak at 663 cm^{-1} caused by vibration associated with defect of oxygen vacancies ≡Si-Si≡, which disappears with the thermal annealing caused by a more ordering of Si-O network [15, 16].

Figure 2 also shows that the Si–O stretching band before and after annealing can be decomposed in a sharp band centered near 1102 cm^{-1} and 1104 cm^{-1} respectively, and a shoulder located at around 1141 cm^{-1}. These bands are attributed to the in-phase and out-of-phase motion of the oxygen atoms [12]. The main IR absorption band of SiO_2 film with the maximum position at 1100 cm^{-1} after annealing shifts slightly to the high frequency region 1104 cm^{-1}, with a diminution in its area. This behavior is mainly associated with the change in phase composition of silicon oxide due to annealing. The ratio of the shoulder height versus the height of the maximum (R=x/y) (see figure 2) has been used to characterize the high frequency shoulder. As reported by E. San Andrès et al [12], when the (O/Si) ratio of the films decreases from the stoichiometric value (O/Si=2), a shift of the stretching band to lower wave numbers, as well as an increase in *R* has been observed.
The full width at half maximum (FWHM) of the Si–O stretching band is shown in Table 1. This parameter is related to the statistical distribution of different bonding environments, so that a lower value of the FWHM means a lower dispersion of local environments and a higher structural order of the film [12, 17]. One can see from table 1 that the sample's pre-annealing present a FWHM = 46.01cm^{-1} and after annealing this parameter decrease to the value of 39.58 cm^{-1} indicating that Si-O network becomes more ordered [18]. It can be seen, also that after annealing we have a decrease in peak height of Si-Si bond from the value of 0,704 cm^{-1} to 0,525cm^{-1}, this behavior can be related to a diminution of Si dangling bonds, however a diminution of amount of paramagnetic defects [18], because the amount of light absorbed is proportional to the concentration of atoms forming the bond [19]. No change in the ratio (R) was observed before and after annealing, suggesting that annealing undertaken did not influence the stoichiometry of the oxide layer.

Table 1. Different parameters deduced from FTIR spectra

Parameters	$SiNx/SiO_2$ Thermal	
	Pre-annealing	Post-annealing
FWHM	46,01 cm^{-1}	39,58 cm^{-1}
R = X/Y	1,034	1,032
Peak Height from Baseline Si – Si bonds	0,704 cm^{-1}	0,525 cm^{-1}

3.3. Hot probe investigation

Currently it is well known that the high density of fixed positive charges within the SiO_2 layer induces an inversion layer at the surface of p-type Si cells, producing a poor surface passivation.
A quick and easy way to detect the presence of an oxide induced an inversion layer is to measure the conductivity type of the sample's surface after oxidation and using the hot probe method [8]. In this measurement, one hot probe and one cold probe are contacted to the sample. The thermal gradient generates a current in the semiconductor, and depending on whether the semiconductor is n-type or p-type, the current will be negative or positive. So, the hot probe method is very useful technique to quickly determine whether there is an appearance of an inversion layer [20].
The results of the hot probe method on our samples with the double layers passivation $SiNx/SiO_2$ show the apparition of an inversion layer leading to switching the surface to n-type. The inversion layer is originating from the positive charges in the film, which is attributed to the E centers and K centers of Si–O tetrahedra (for SiO_2) and Si–N bonds (for SiNx) respectively, leading to passivation degradation [21 -23].

3.4. Optical characterization

As the double layer $SiNx/SiO_2$ is intended to be used in solar cells, aiming to ensure a good passivation and anti-reflection coating, we have done an optical characterization of the prepared layers using spectrophotometer technique. The obtained results for the samples after annealing in reflection mode are presented in the figure 3.

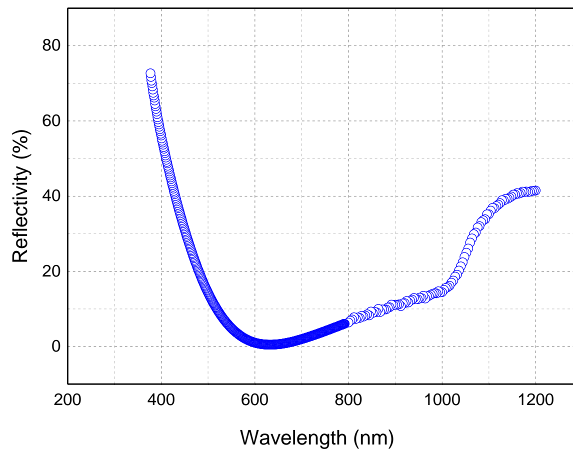

Fig. 3: Reflectance spectra for SiNx/SiO_2 under normal incidence on p- type CZ <100> non texturized wafer

It is well known that the maximum of solar radiation is for a wavelength of approximately 600 nm which should correspond to the minimum reflectivity of the deposited layers. In our study the double layers SiNx/SiO_2 present V-shape reflectivity with a minimum at the specific wavelength of 600 nm with a weighted reflectance (WR) of 10,79% evaluated over the AM1.5G solar spectrum (Air Mass 1.5 Global: terrestrial solar spectral irradiance on a surface of <100> orientation under standard atmospheric conditions) in the wavelength range 400 – 1100 nm on non-texturized wafer. Our calculations of WR clearly show that SiNx/SiO_2/p-Si double-layer is suitable for antireflection film (ARC) for solar cell.

Conclusion

The passivation properties of SiNx/SiO_2 stack on p type <100> Cz c-Si has been studied based on the carrier lifetime, Optical reflectance, chemical bonding, and the presence of fixed oxide charges inducing an inversion layer. The dual layers SiNx / SiO2 are intended to be used in solar cell surface passivation. Despite the good performance in terms of optical response, SiO_2 does not seem to be suitable for an effective chemical passivation because of the Si-Si peak, which remains rather high, indicating a large concentration of paramagnetic defect proved by a τ_{eff} of the order of 16 µs which remains a rather weak value compared to the single SiNx layer, this weakness is relative to the primer of the inversion layer at the SiO_2 /p-Si interface favoring (O_3-Si) defects originated principally from the E centers due to the high positive charges in the SiO_2 film. We have also shown that annealing at 400°C under 25mTorr can provide an enhancement in the surface passivation by minimizing the surface recombination at the interface.
In conclusion, it seems that SiO_2/SiNx passivation may be more efficient on n^+ / p structure or n-type substrates.

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