Surface modification by pulsed plasma treatment of silicon wafers for solar cell application

I. Rosales, H. Martinez, R.Guardian

Abstract— **Silicon wafers were modified by the application of two consecutive surface treatment namely ion nitriding and Ti deposition (by physical vapor deposition) followed by an annealing heat treatment. SEM/EDS line scan analyses determinate that nitrogen diffusion was close to 4 µm while titanium diffusion acquired approximately 2 µm maximum. Fractographic analyses by SEM have shown that effectively exist morphological modification below the surface wafer. Modeling studies carried out using the present experimental data, reveal that nitrogen flux concentration produces a similar diffusion behavior added in stationary and no stationary state.**

Index Terms— **Diffusion; Solar cell; Energy**

I. INTRODUCTION

Applications such as solar cells fabrication result the most popular use for silicon wafers which generally are produced by Czochralsky method (pulling). Silicon wafers are chemically cleaned and using a diamond saw, are usually cut along a {100} plane. It is important to take into account the wafer surface preparation, because the best efficiency can be obtained with a correct surface finishing treatment, in order to reach the best antireflection property. In this aspect, chemical surface treatments has been applied with excellent results [1].Thermal defects such as vacancy concentration can be developed during the melting and solidification of the crystal for such reason it is well known that nitrogen doping has been widely used to control the voids generation in silicon crystals [2-4]

Since nitriding reaction not only occurs at the surface, also occurs simultaneously in the subsurface due to the continuous atoms diffusion from the nitrogen source. Thus, diffused nitrogen inward the silicon wafer, can primarily react with silicon atoms, generating a fine dispersed nitride layer which possesses an improved density with lower porosity level. Therefore the main purpose of the present investigation is to provide information about the possibility of generate a nitrided layer with a subsequent PVD-titanium deposition to produce an optimal surface, with silicon nitride and titanium dioxide which can be ready to be used as a reinforced antireflection layer for solar cell application.

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II. EXPERIMENTAL PROCEDURE

Silicon wafers supplied by a commercial vendor (99.9999% purity), were used to perform this study. Surface samples were pre and post treated by the application of a bath consisting in hydrofluoric acid (50%) in isopropyl alcohol for 10 minutes, in order to obtain a better surface texturing. After this treatment, samples were thermo-chemical treated by a AC, 60 Hz generator for 6 h at 500 ± 10°C, 360 ± 15 V, 75± mA and a constant pressure of 1200 ± 40 Pa adjusted with mass flow meters. The gas composition used for the nitriding tests was 20% N_2–80% H_2. Ti-deposition was performed in a Polaron SC7020 PVD machine with a Titanium plate for a 6 h of deposition time, after that, annealing heat treatments were carried out under air atmosphere for a 12, 24 and 48 h at 950°C. Analyses of the surface sample and cross-section fractographic images were performed in a LEO-1450VP scanning electron microscope (SEM). In addition, line-scan chemical analyses were performed using the Energy Dispersive X-Ray Spectroscopy (EDS) system of the equipment. Modeling of the nitrogen and titanium diffusion was carried out based on the no-stationary Fick´s law.

III. RESULTS AND DISCUSSION

3.1 SEM analyses

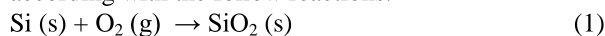
3.1.1 Surface Morphological Evaluation

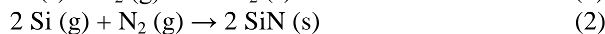
Because silicon wafers need to be exposed to an etching process to obtain an effective antireflection surface, thereby it is important that surface sample after the treatment process does not get an excessive distortion for the subsequent texturing chemical treatment [5,6].

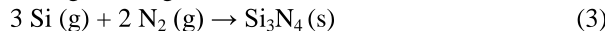
Figures 1a to 1c shown the SEM surfaces images of the samples in annealing condition after treatment of ion nitriding plus PVD-Ti deposition at 12, 24 and 48h, respectively. It is observed in Figure 1a that surface appears with excessive flat regions (≈ 40 μm^2), therefore, it was determinate that sample treated with 12 h, it do not present a morphological change, which means that the applied treatment time is not enough to produce an adequate surface texturing. For the case of the sample with 48 hours of treatment, that result with marked affectation on the surface mainly in the precipitate formation oxides and several zones with some porosity degree which may affect the continuous and homogeneous surface morphology.

However, in Figure 1b, it can be observed the surface of the sample with 24 hours of treatment, which showed a regular surface texturing appearance, with minimal micro-voids and excessive clusters particles presence, also it is clear that original flat zones disappeared, although the possibility to obtain a thermally as grown Si-SiO_2 interface is high, mainly due to the presence of oxygen in the atmosphere [7].

After the annealing treatment, silicon surface is protected by an unstable thin layer of silicon dioxide, SiO_2. After this, reaction with oxygen in the air produce a stable silicon dioxide. On the other hand, high temperatures silicon reacts with nitrogen, N_2, which in our case come from the ion nitriding process, to form the silicon nitrides SiN and Si_3N_4, according with the follow reactions:

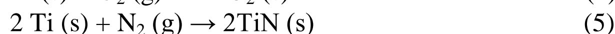

$Si\,(s) + O_2\,(g) \rightarrow SiO_2\,(s)$ (1)


$2\,Si\,(g) + N_2\,(g) \rightarrow 2\,SiN\,(s)$ (2)


$3\,Si\,(g) + 2\,N_2\,(g) \rightarrow Si_3N_4\,(s)$ (3)

Titanium addition by PVD, cover the ion nitrided silicon surface, then once titanium starts to heating up in air, it start to get reaction with the present elements and the oxygen present in the atmosphere to form titanium dioxide (TiO_2) and titanium nitride (TiN) as is indicated in the reactions:

$Ti\,(s) + O_2\,(g) \rightarrow TiO_2\,(s)$ (4)


$2\,Ti\,(s) + N_2\,(g) \rightarrow 2TiN\,(s)$ (5)

Equations 1 to 5 describes the chemical reaction of the silicon wafer with the elements added in the treatment, considering the oxygen presence to generate the oxides in the wafer surface, in order to acquire the adequate index reflection by surface texturizing, moreover, with the creation of titanium oxide nanostructured, good response can be obtained to generate luminosity intensity and excellent conversion energy rate in electricity.

3.1.2 Cross-section crystal evaluation

It is proposed that the nitrogen diffusion process begin with the surface atoms saturation, then, nitrogen migration flux inside the substrate starts to react with the silicon atoms until a new barrier of atoms saturation is produced; this process occurs successively, while the temperature and atom concentration promotes the diffusion process.

Fractographic image of the sample treated with 24 h is presented in Figure 2, the image shows that the produced layer is uniform below the surface sample with an average of 4µm depth. It is observed that during the fracture process, the sample split off in two sections, creating a series of irregularities very well defined with several grooves, which are produced from the surface sample to the end layer; this behavior was not expected, because silicon wafer possesses a high hardness (1150 kg/mm^2) thus, it is expected a fragile fracture with the apparition of flat zones characteristic of a brittle material, therefore it is postulated that the performed treatment has affected the surface morphology and thereby the fracture observed has been modified creating potentially new paths for luminosity trapping.

Sample with 24 h of treatment was evaluated by SEM line scan analysis, showing that both elements effectively penetrate through the initial surface diffusion zone, as can be observed in the line scan in Figure 3, in first place where nitrogen is detected from the surface sample trough inner sample, reaching a maximum saturation in 3µm approximately below the surface, describing a decrement concentration near to 5 µm. In the case of titanium diffusion, it was observed in figure, that radiation is quite low in comparison with nitrogen which present higher intensity, it is observed also that the minimum concentration occurs at 3 µm below the surface and the maximum in the top sample (marked by an arrow). The explanation for this diffusion behavior can be found by considering that if silicon single crystal lattice parameter is 5.431 Å, with an atomic radii of 1.46 Å and a distance between the nearest neighbors atoms in the lattice equal to 2.351 Å, then , the nitrogen flux underneath is easy to carried out, due to the atomic radii for nitrogen is 0.76 Å, therefore, exist enough space to permit that nitrogen can be introduced interstitially inner the cell during the thermochemical treatment; for such reason the diffusion profile for nitrogen in Figure 3, it is observed with a high intensity below the surface; contrary to the case of titanium that possesses an atomic radii of 1.47 Å (very similar with silicon atomic radii), thus it is more difficult the diffusion process in comparison with nitrogen diffusion, considering that nitrogen was previously introduced into the lattice by ion nitriding technique, which may reduce the interatomic spacing, therefore, when titanium is pretended to diffuse inner the silicon crystal structure there are limited spacing to diffuse in a interstitial way, thereby the proposed diffusion mechanism for titanium during the treatment is basically substitutional type.

IV. Diffusion Modeling

Values of titanium and nitrogen concentrations were obtained from chemical punctual analyses performed below the treated surface in sample with 24 h of treatment (annealed); this experimental data, has been used to obtain information about the diffusion behavior under different conditions such as stationary and no stationary flux of N_2-H_2 mixture gas introduced in the reactor chamber. In Figure 4a and 4b, are presented the compositional profiles for Ti from the surface to the interior of silicon wafer (note that titanium was deposited after ion nitriding) in stationary and no stationary condition, respectively. These profile curves provide the possibility to predict the corresponding diffusion processes and the corresponding Ti layers formation, it is observed that the diffusion is very limited at only 1µm approximately below the surface sample, while in Figures 5a and 5b where are shown the diffusion profiles for nitrogen in stationary and no stationary condition respectively, it is observed that the diffusion is carried out until 4 µm approximately in good concordance with the line scan analyses. From the analysis of the obtained results, it was observed that Nitrogen concentration is approximately 100 times bigger in comparison with the Ti-concentration.

The diffusion coefficient or diffusivity was obtained by fitting the experimental results with the mathematical solution of the partial differential equation that describes non-steady-state diffusion, under the knowledge that the diffusion coefficient (*D)* is assumed to be constant. Therefore, the mathematical solution is given by the Gaussian function (GF) profiles

$$c(x) = \frac{c_0}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt} \right),$$

where c(x) is the concentration at x distance from the surface, c_0 is the concentration at the surface, and t is the treatment time.

From the predicted figures, it can be observed that the GF profiles fitted to the experimental results as solid lines. That fitted were found with a correlation factor of 0.93, which ensure the reliance of the fit. Since the GF are tabulated as a function of the argument $x/\sqrt{4Dt}$, the value of the diffusion coefficient could be obtained. Using this relation, in Table 1 are presented the calculated values for the diffusion

coefficient for each element, namely nitrogen and titanium. In which are included the areas of the GF profiles fitted to the experimental data, where a semi-quantitative analysis was used for this calculations. Analyzing the results in table, it can deducted that exist higher diffusion of N than Ti in the sample, which can be confirmed by the ratio between areas, $A_N/A_{Ti} \approx 178$. It means that the N diffusion was more effective than the Ti diffusion. This behavior can be explained due to the initial temperature condition reached in the ion nitriding treatment which promotes N diffusion to the silicon matrix, while Ti deposition do not get a primary temperature affectation. Therefore, the annealing treatment permit the diffusion process for both elements, however due to nitrogen atoms has occupied the majority of the free sites of the silicon lattice, then it is more difficult for titanium atoms to diffuse to the inner sample, reaching less than 1µm below the surface.

V. Conclusions

Silicon wafer were thermochemical treated by ion nitriding and PVD –Ti deposition followed with an annealing treatment. Surface sample observation reveal that the optimal time to be applied result to be at 24 h. Diffusion results have indicated that nitrogen present a better diffusion performance into the silicon wafer in comparison with titanium. This behavior it is attributed mainly due to the differences in atomic radii. It was stablished that there are not significant differences in diffusion behavior with stationary and no-stationary nitrogen flux. X-ray diffraction studies are currently being developed and the next step of this research will be to assembly a solar cell to observe the efficiency produced by this process.

Acknowledgments

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Figures

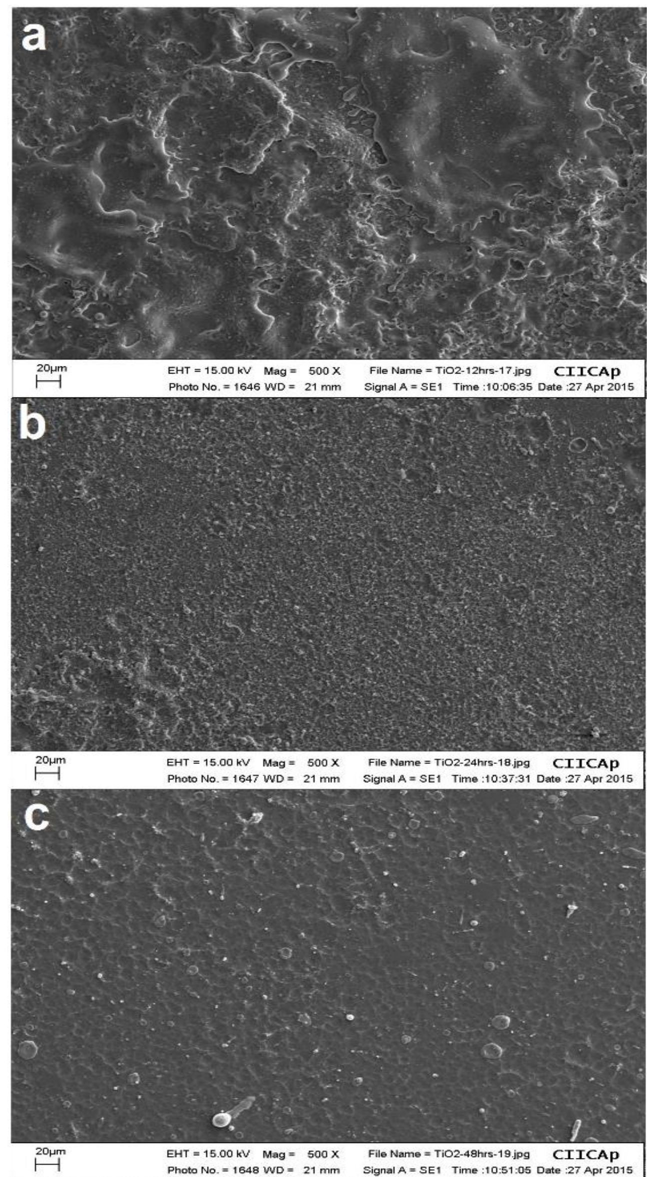

Figure1. Images of the surface samples after treatment, at the same magnification and work distance at the treatment time of. a) 12 h, b) 24 h, c) 48 h.

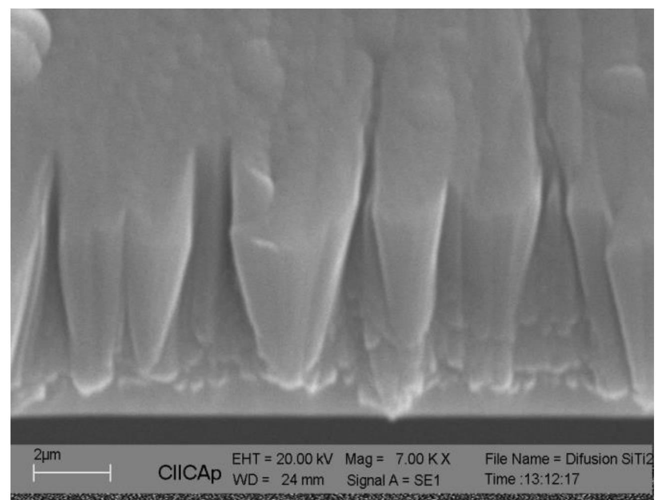

Figure 2. Cross-section fractografphic image of the silicon wafer treated for 24 h, is observed the grooves and the irregularities produced from the top to the inner sample.

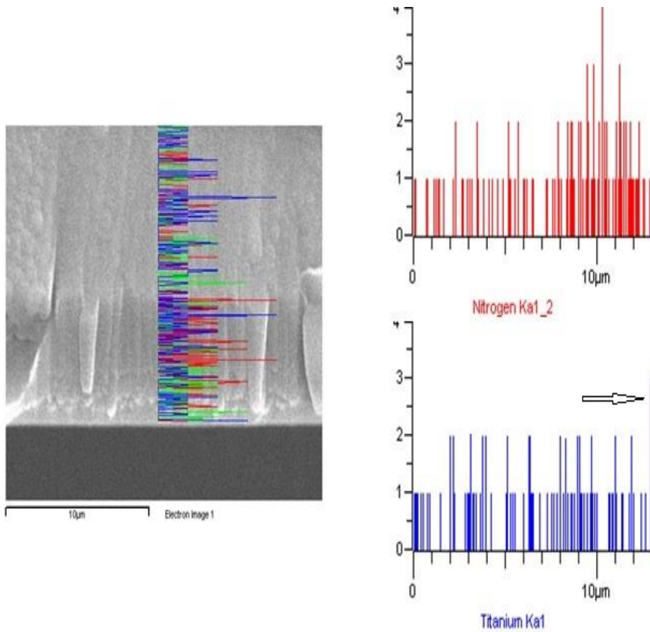

Figure 3. SEM/EDS lines scan image of the sample treated for 24 h, showing the nitrogen and titanium position below de surface.

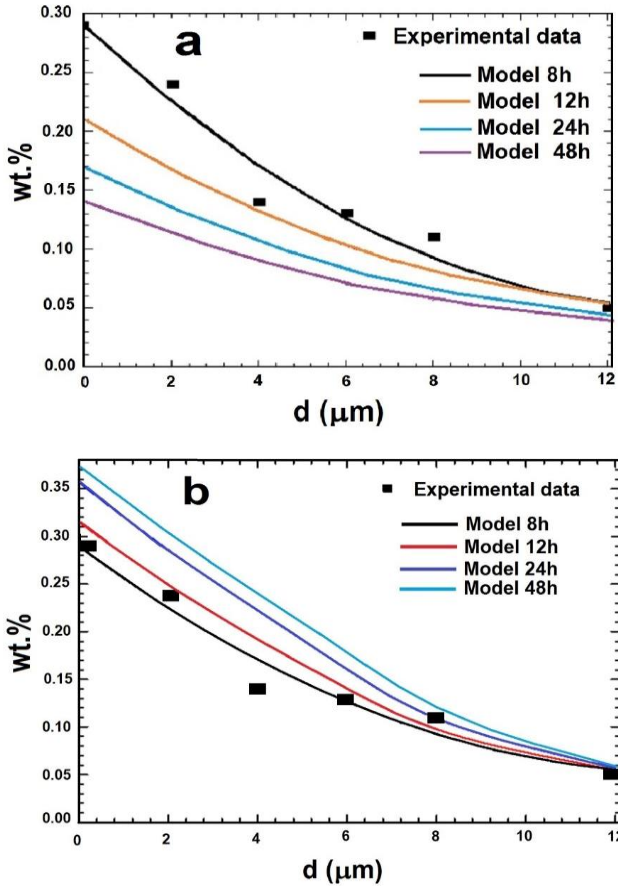

Figure 4. Model of diffusion profile for nitrogen with a) stationary nitrogen flux after the process b) no-stationary nitrogen flux after the process

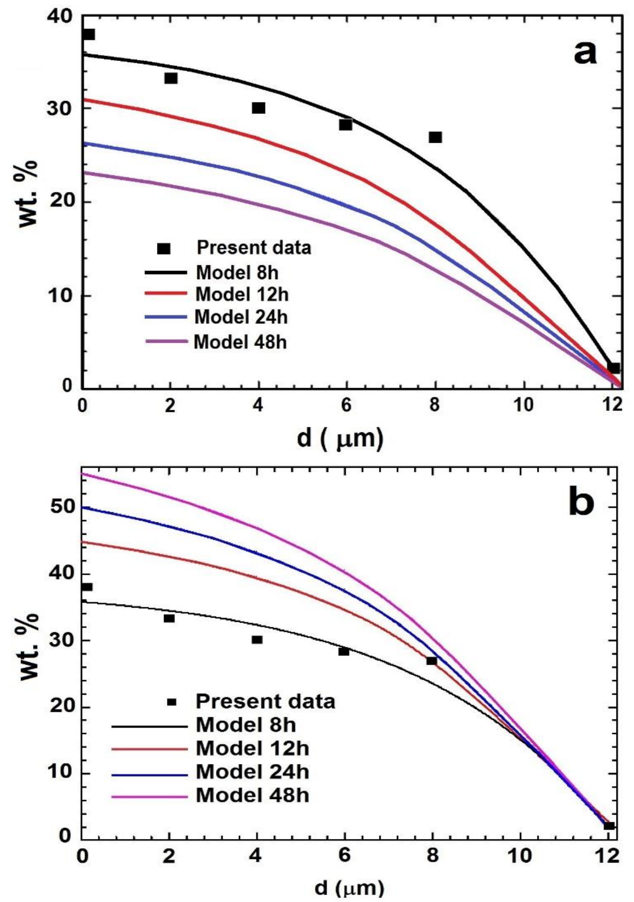

Figure 5. Model of diffusion profile for titanium with a) stationary nitrogen flux after the process b) no-stationary nitrogen flux after the process.

Tables

Element	Diffusion coefficient (10^{-17} m^2/s)	Area (wt.% x 10^{-6} m)
N	6.93	304.15
Ti	0.017	1.71

Table 1. Values of the diffusion coefficients for nitrogen and titanium for the sample treated at 24 h.