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Etching, Evaporated Contacts and Antireflection Coating on Multicrystalline Silicon Solar Cell

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Abstract- This work has focuses on the development of a simple and low cost alternative to these deposited coatings (ARC) , through the use of an electrochemical etching technique to form AR layers of silicon (mc-Si). This is considered as the proper etching process for mc-Si. Also, silicon oxide (SiO) and titanium oxide (TiO_2) coatings have been used to reduce the reflection losses from silicon solar cells. More than 20.6% enhancement in the short circuit current has been demonstrated in the polished cells using evaporated SiO antireflection coating. Additionally more than 12% enhancement in the short circuit current has been observed after TiO_2 antireflection coating. The output current is found almost directly proportional to light intensity.

Keywords- ARC, electrochemical etching technique, multicrystalline Silicon Solar cell, reflection losses, polished cells.

1. Introduction

Silicon photovoltaic has several features which make it attractive for. Solar generators simply transform the sunlight into electricity. The consumers of this energy are not normally connected with the generator. They get the solar electricity after preparing and adapting it to the consumers needs in a current/voltage converter. The system consists of what is called photovoltaic energy supplying system (PVE). The active working device of this system is the solar cell.

Multicrystalline silicon based devices dominate the present solar cell industry due to their durability, their relatively low cost, and the vast silicon data base developed by the microelectronics industry. However, the high refractive index of crystalline silicon at solar wavelengths (approximately 3.5) creates large reflection losses that must be compensated by applying antireflective coatings (ARC). Although highly efficient, double and triple layer AR coatings are available; most manufactured crystalline silicon photovoltaics employ simple and inexpensive single layer ARC, with relatively poor AR properties.

On the other hand, photo-resist liquid phase (PLP) is a suitable silicon deposition process for fabrication of thin film silicon solar cells. In this paper we discuss the design and operation of a batch system which is a first step towards mass production. Silicon photovoltaic has several features which make it attractive for. Solar generators simply transform the sunlight into electricity. The consumers of this energy are not normally connected with the generator.

We have now focused our investigation on the use of mc-Si wafers for ARC applications. By isolating these layers in the heavily doped surface region of a solar cell, the electrical properties of the p-n junction are relatively unaffected. Provided that good electrical contacts can be made to the material under the porous layer, the electrical properties of the P-Si film are not critical, and only the optical properties need to be optimized.

There are many methods for detecting and characterizing defects in a multicrystalline solar cell's surface. Etching is one of them. As it is known, etching and polishing were used as more suitable methods for solving problems concerning the mentioned defects. In line with results of a recent investigation obtained by H. J. Möller et al [1] on uses of SiO and TiO_2 as antireflection coatings (ARC) in simplified processing for multicrystalline silicon solar cells, SiO and TiO_2 coatings were evaporated to reduce the reflection losses from solar cells. The structure was characterized by optical reflection and a simple formula for the use of wavelength. In this work the use of evaporated SiO antireflection on polished cells are more than 20.6% enhancement in the short circuit current has been demonstrated and more than 12% enhancement in the short circuit current has been observed after TiO_2 antireflection coating. Defects such as grain boundaries and dislocations can easily be made visible via a selective etching on the polished surfaces.

Multicrystalline silicon with random orientations of the grains etchants are necessary so that etch defects independently of the surface orientation. This problem is less severe for grain boundaries, dislocations and large precipitates. In general, it is very difficult for multicrystalline silicon to obtain qualitative results on the density and distribution of defects compared to mono-silicon [1]. An obvious requirements for high efficiency in photovoltaic modules to be low reflectance and for multicrystalline silicon solar cells to achieve low reflectance is through use of antireflection coatings with area for multicrystalline silicon wafers 10 x 10 cm^2. Because of the desired range of the reflective index (n) of the selected antireflection coatings is from 1.4 to 2.7, SiO and TiO_2 are more suitable for this purpose. This range includes SiO, SiO_2, Si_3N_4, TiO_2, Al_2O_3 and Ta_2O_5 [2-7]. The chemical vapor deposition (CVD) and silk screen have been the most promising techniques used for the deposition of TiO_2, SnO_2, ZnO_2, Ta_2O_5, and other antireflection layer [8,9], and some manufacturers have incorporated these processes in their production lines. The deposition of antireflective coating on surface through direct liquid spraying has not been reported yet.

In this work, SiO, and TiO_2 were evaporated and sprayed to be deposited on silicon as antireflection coatings. This process was carried out on solar cells after making front, as well as back contacts. Also moreover important measurements have been carried out and discussed in this work concerning the enhancement in short-circuit current (I_{sc}) of the multicrystalline silicon solar cells.

2. Basic Principles

The conversion of light into electricity in a solar cell is dubbed the photovoltaic effect. For its occurence and use, it is necessary to have a material in which the following contains elements : the free positive and negative carriers are created by the absorption of the light, a device with an internal field which separates the generated carrier pairs, an-An appropriate contact at the surface of the device through which the current can flow to the consumer.

The first requirement is fulfilled by all semiconductor materials. The internal field can be produced by connecting materials with different work functions. The possible combinations are p-n junction devices, hetrojunction devices, respectively SIS devices, Schotky junction devices, respectively MIS devices. The third requirement demands finding a contact material which enables the carriers to take off from the cells with a minimum of power loss.

The current/voltage characteristic of an illuminated solar cell is a superposition of the dark current/voltage characteristic and the current generated by the incident light. Three points of this Current/voltage characteristic determine the properties of a solar cell: The short circuit (equivalent to light-generated current), the open circuit voltage and point of maximum extracable electrical power. The short circuit current is detemined by the light intensity, its spectral distribution and the perfectness of the crystal and the impurity concenteration in the crystal.

The open circuit voltage is given by the properties of basic material (its band gap), the dark current/voltage characteristic of the device and the operation temperatures. The ratio of the maximum power output and the product of short circuit current and open circuit voltage is the curve factor of the fill factor. The ideal value of this factor is determined by the dark current/voltage characteristic. The most important parameters of a solar cell is its efficiency of energy conversion. It is given by the ratio of the maximum electrical power output and the solar power input. It depends on the intensity of the light, its spectral cell design, and the operation temperatures. In the real solar cell some power loss factors are incorporated. In principle they could be made as small as desired, but practically it is different because of the lamination of the material parameters and the technology. Thus improvement the performance of a solar cell means setting optimum comprises between coating parameters.

Although the crystalline and multicrystalline silicon are not there optimal material for sunlight conversion, the crystalline and multicrystalline silicon solar cell with pn-junction is the unique cell type which is produced in big amounts. Its application in many pilot projects has proven in self supporting power stations up to some hundred kilowatt. The reason for the usage of silicon for solar cells are given by its unlimited availability, low pollution problems during the cell manufacturing, and the high developed technology for all silicon devices. A solar generator is built up by connecting different cells. The voltage of a generator is given by a number of cells that connected in serially. The maximum current is given by a number of parallel connected cells.

More than 35% of the incident light is reflected back from a bare silicon surface, which can be effectively utilized by using a desired ARC for keeping the occurred reflection to its minimum value. For a single layer ARC and in the normal incidence conditions, we can use the following relation [1]:

$$\lambda_0 = 4n_1d_1 \tag{1}$$

Where, n_1 and d_1 are the refractive index and the thickness of the ARC respectively, and λ_0 is any wavelength. The reflectance R of the top surface of a solar cell is given by [2]:

$$R = \left\| \left(n_1^2 - n_0n_2\right) / \left(n_1^2 + n_0n_1\right) \right\|^2 \tag{2}$$

Where n_0 and n_2 are the refractive index of the medium above the ARC, (air in the present case), and that of the substrate below the ARC respectively. For zero reflectance, i.e. R = 0, therefore Eq. (2) becomes:

$$n_1 = \left(n_0n_2\right)^{1/2} \tag{3}$$

At λ_0, the optical thickness n1 d1 of the layer is equal to one quarter of λ_0. This is called a quarter wavelengths ARC (QWAR). The Selection of ARC materials depends on the ease of deposition, refractive index, controllability of thickness uniformity and the property of the coating. Consequently, SiO is a good candidate for ARC on silicon solar cells (refractive index {1.9}), TiO_2 {2.25}.

3. Experimental

Cleaning and etching processes are used to selective removal of the organic and inorganic materials from patterned and unpatterned substrate surface. When a process is used to remove particulates or unwanted films, it is called cleaning. When a film which is used intentionally deposited or grown is removed, the process is called etching process which used in the solar cells devices. We used chemical cleaning based on hot alkaline or acidic hydrogen peroxide (H_2O_2) solutions, to remove the chemically bonded films from the wafer surface, using the solution of (HN_4OH : H_2O + HCL : H_2O_2). This solution is very effective in removing organic contaminates.

The HN_4OH dissolves organic films and also complex of Group I and II metals such as Copper, Silver, Cobalt, Cadmium, and Nickel. H_2O_2 + HCl : H_2O solution is effective in removing the heavy metals. Sulfuric acid H_2SO_4 and mixtures of H_2SO_4 + $(NH_4)_2$ S_2O_8 used to clean the wafer from organic materials.

Etching is the selective removal of material, either locally where windows are defined, or over the entire wafer without patterning. At least one etching step is performed during the manufacture of solar cells devices. We used more solution or polishing solution of rough silicon surface. Etching polysilicon is similar to etching single crystal silicon, in most cases, however the etching rate is considerably higher because of grain boundary effect, and it is necessary to modify the etch solution to reduce it and make sure that the etchant does not severely attack SiO_2. The HF/HNO_3 solution is diluted with water or acetic acid to increase the polysilicon/oxide etch rate and depending on the grain size. For doped polysilicon, the etch rate typically increase as the dopant concentration increases and the grain size decreases. Phosphorus has more rappid affecting more than arsenic and boron on the etch rate. A typical etchant of polysilicon is a solution of potassium hydroxide (KOH). Another etching of polysilicon is NaOH. The cleaned and polished samples should be characterized by two methods, the first method is to compare their reflection capability for direct incident light with an optically polished silicon surface. This measurement is taken by spectrometer. The second method is a visual inspection by a light microscopy with the availability to take digital pictures. We take three pictures for each sample with a magnification constant for all samples and suitable to resolve the etch structure.

Metallic patterns were formed on the highly n-type Emitter of solar cells prepared from mc-Si. The metallization was done by evaporating either Al or a Cr layer followed by a Cu layer onto the samples. The evaporation was done in a vacuum chamber with a residual total pressure of about 5x10-6 mbar. The main residual gas was water vapor. Al and Cu were thermally evaporated whereas Cr was deposited from a crucible-free electron gun. No further heat treatment was applied. In order to structure the deposited metal, two methods were used. In the first method- referred to as etch away process in table-1, the metal was evaporated directly onto the sample surface and then covered by a photolithographically applied mask. Unconverted areas were etched away with HF in the case of Al. In the lift off process the sample's surface was covered by a photolithographic mask and subsequently coated with the metal. After coating the metal on top of the resist, the photolithography was done by coating the wafer with a positive developing photoresist which was applied to the samples by the use of a spinner. The light exposure was performed by contact masks. They presented the samples prior to processing. A summary of the preparation conditions is given in Table 1 (Appendix). A schematic representation of p-n junction solar cell is shown in Fig.1(c). It consists of a shallow p-n junction formed on the surface, a front ohmic contact stripe and fingers, a back ohmic contact that covers the entire back surface, and an antireflection coating on the front surface. A back ohmic contact that covers (Al+Ag) the entire back surface, and an antireflection coating on the front surface.

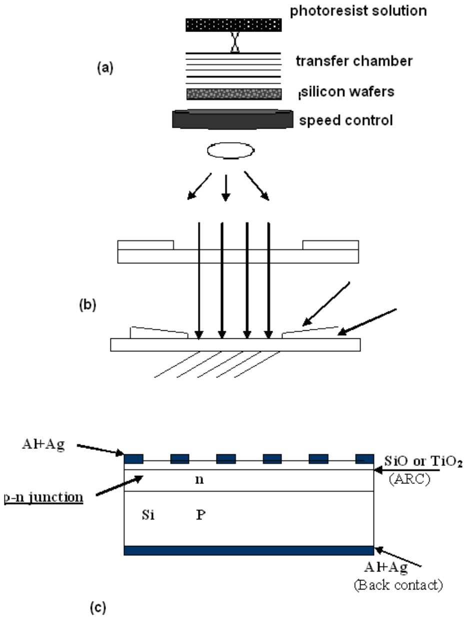


Fig. 1. Measument system, a) Schematic of the batch system PLP, and b) Generic optical lithography system, and c) Structure of the solar cell used the characterization.

Fig. 2 the finally processed sample m20 is shown. The upper part was covered with copper, the lower part with Al. The sticking of the metals onto the surface was acceptable desepite bening striped off with a Tixo tape {2} Due to the surface topography caused by etching step prior to diffusion we were unable to lift off the photoresist/metal buried in narrow grooves {1}. The method to determine the contact resistance was to compare the four terminal resistance with two terminal resistance of the inner two contacts. Since in the four terminal configuration, the inner two contacts used to measure the voltage are current less the measured resistance corresponds merely to the highly doped emitter of the solar cell. The current through the sample was varied between -0.1 A and +0.1 A. Using, the 2 terminal configuration the 2 metal/semiconductor transitions represent a resistance in series to the sample resistance thus leading to an additional voltage drop which was recorded. This method assumes that the sample resistance determined by the current path in the sample remains unchanged when switching from the 4 terminal. Our sample geometry does not fulfill these criteria. However they allowed us to statistically evaluate our result due to the opportunity to measure locally the contact resistance. The contacts under test in sample m20 are marked by lines (3a-d and 4). In each line 4 subsequent contacts were externally wired by either pasting Cu wires with a conducting epoxy bonder or by soldering{4}. The contacts under test were permutated along the line.

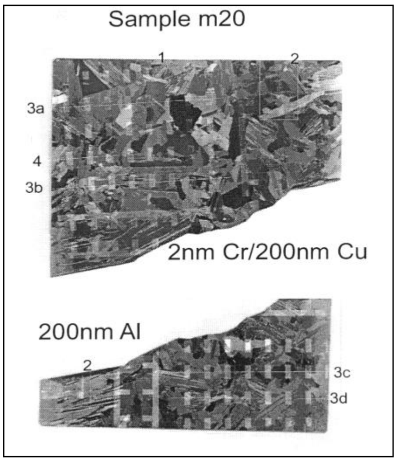


Fig. 2. Photo of sample m20 as follows:-

1) Example of sharp edged grooves where the photoresist and the metal could not be remove.
2) Locations used for testing the metal sticking onto the surface with a Tixotape.
3) Locations used to evaluate emitter and contact resistance (external wire connections are pasted silver epoxy).
4) Location with soldered connections

The next step is obtaining a digital image of reflectivity of the front surface of the silicon wafer to calculate a finger grid of metal lines that follow the grain boundaries wherever possible. In this work SiO or TiO_2 antireflection coating was deposited on silicon by evaporation and spray.

The solar cells used for measurement are 100 cm^2 multicrystalline silicon cells with submicronic junction..

4. P-N Junction Solar Cell

When the cell is exposed to the solar spectrum, a photon that has energy less than the bandgap Eg makes no contribution to the cell output. A photon that has energy greater than Eg contributes an energy Eg to the cell output Energy greater than Eg is wasted as heat. To derive the conversion efficieny, we shall consider the energy band diagram of a p-n junction under solar radiation. The source IL results from the excitation of excess carriers by solar radiation, I_s is the diode saturation current, and R_L is the load resistance.

The ideal I-V characteristics of such a device are given by:

$$I = I_s\left(e^{V/KT} - 1\right) - I_L \tag{4}$$

And

$$J_s = {I_s}/{A} = qN_C N_V\left[{1}/{N_A}\sqrt{\frac{D_n}{\tau_n}} + {1}/{N_D}\sqrt{{D_p}/{\tau_p}}\right]e^{-{E_g}/{KT}} \tag{5}$$

Where A is the device area, the curve passes through the fourth quadrant, and therefore power can be extracted from the device. where I_s is the diode saturation current, the constant-current source is in parallel with the junction (which results from the excitation of excess carriers by solar radiation).

5. Result and Discussions

Fig. 3 the calculated contact resistance (contact is 2 times 10 mm^2) is plotted against the sample resistance for all our measurements. At the current state, no difference between Cr and Cu metallization was found. Both metals exhibit an ohmic, current independent transition. The influence of a chemical post-treatment of the surface is not clear. neverthless to some degree there seems to be a correlation between the local emitter resistance and the contact resistance. The method to determine the contact resistance will be improved. The major problems in further improving the contact resistance at the moment arise from the uncertain chemical and rough topographical nature of the sample's surface.

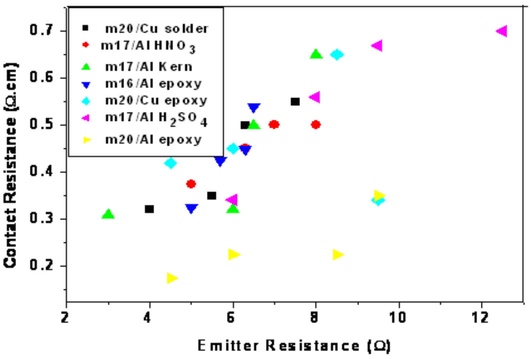


Fig. 3. Calculated contact resistance vs. the sample emitter resistance.

When the cell is exposed to the solar spectrum, a photon that has an energy less than the bandgap Eg makes no contribution to the cell output. A photon that has an energy greater than Eg is wasted as heat. To derive the conversion efficiency, we shall consider the energy band diagram of a p-n junction under solar radiation, shown in Fig.1(c) , the ideal I-V characteristics of such a device are given by Eq. (4)

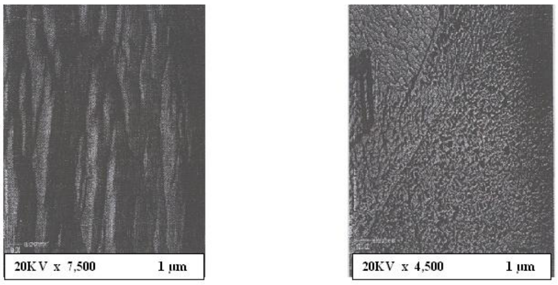


Fig. 4. Optical micrograph of an etched surface showing grain boundaries and dislocation.

A typical optical of an etched surface is shown in Fig. 4 and shows grain boundaries and an inhomogeneous distribution of dislocation; but it appears that the grains grow without any texture.

The ARC effect relies on a destructive interference of waves reflected at the top and bottom of the coating, which results in a very low reflectance (R_{min}) at a certain wavelength (λ_{min}). This effect lowers the reflectance in a wavelength domain centered on λ_{min}, which for photovoltaic application must lie between 650 and 700 nm (as shown in Fig.5), where the energy contact of the solar spectrum peaks are shown. An optimal ARC effect will be achieved under two conditions one of which is related to the refractive index of the ARC material (n_{ARC} d_{ARC})[10].

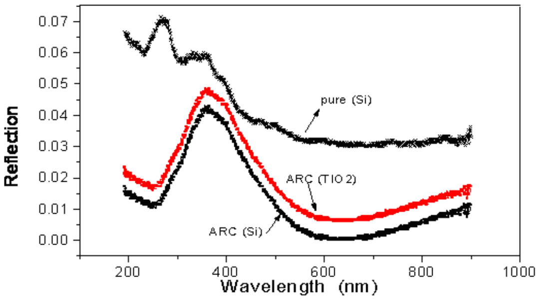


Fig. 5. Reflection versus wavelength of polycrystalline Silicon wafers for pure and ARC (SiO, TiO_2).

The first condition is that the reflected wave amplitudes must be equal to fully cancel each other (R_{min} = 0). When the ambient medium is air (n_{air} = 1), this imposes [11,12]:

$$n_{ARC} = \sqrt{n_{c-Si}^{2}} \qquad (6)$$

where $n_{c\text{-}Si}$ is the refractive index of crystalline Si which depends on the wavelength (0.031 at 650 nm, 0.0307 at 700 nm). According, the reflective index of an optimized ARC material should be equal to .00041at 650 nm and .00127 at 700 nm. The second condition imposes the optical thickness of the ARC to be equal to a quarter of the wavelength (λ_{min}) at which zero reflectance should occur. (i.e. reflected waves must be out of phase by p) [13,14]:

$$n_{ARC}\, d_{ARC} = \left(\lambda_{\min} / 4 \right) \qquad (7)$$

Hence from Eq.(6) and eq. (7) an ARC thickness of 83 nm (90) nm is required to produce a zero net reflectance at 650 nm (700nm). The results of specimen of these experiments are given by Fig. 6. It can be noted that , through the use of evaporate SiO, the short circuit current (I_{sc}) of the solar cells increases, and gives the value 26.05 % enhancement in the short circuit current for the specimen

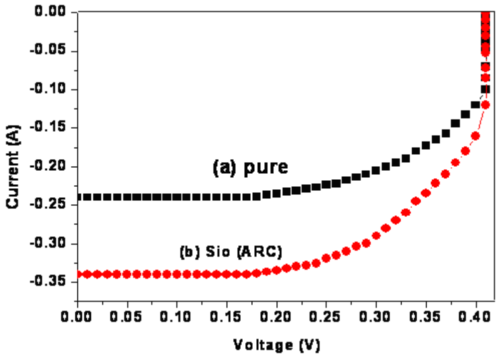


Fig 6. I-V characteristic for mc-Si (a) pure , (b) by ARC (SiO).

Fig. 7 shows the current-voltage curves of the cells. The advantage of using the spray TiO_2 as an antireflection coating on the surface are evident, as observed when compares the short circuit currents and efficiencies of the cells. the efficiency of the cell prepared with (ARC) is higher than that of the cell prepared using a bare silicon surface [15-20]. Coating the cell surface with ARC (TiO_2) improves the performance, the short circuit current increase by 12%.

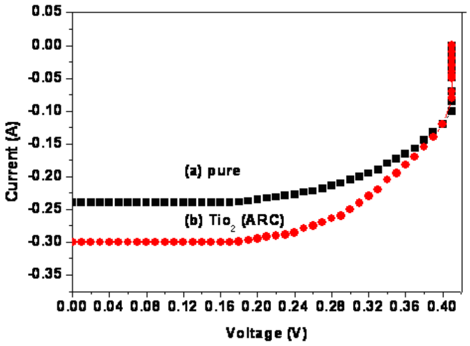


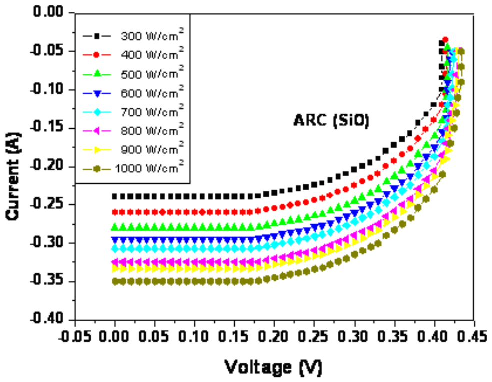
Fig. 7. I-V characteristic for mc-Si (a) pure , (b) by ARC (TiO_2).

The use of chemical evaporate and spray technique, for the deposition of an antireflection coating of SiO, TiO_2 on silicon cells, proved to be efficient despite of characteristic of the deposition technique and of the nature of the silicon surface. The integrated reflectance of the (ARC) structure was reduced to about the same level of the reflectance obtained using antireflection coating deposition by conventional technique.

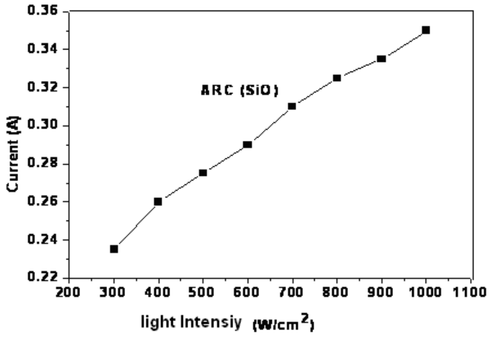
The current through the solar cell due to the incident light depends upon the energy of the incident light as well as the energy gap of the material solar cell [21,22]:

$$I_{illumination} = A \int_{E-E_g}^{\infty} \sqrt{(E-E_g)}\, dE \qquad (8)$$

where A is the area of illumination, and E is the energy of the incident photon.



(a) Current-Voltage characteristic of the cell for different illumination intensities of incident light for ARC of SiO.



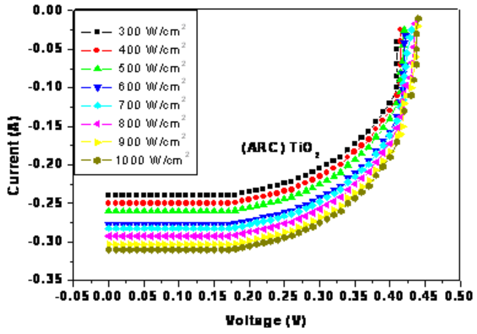
(b) Current-intensity characteristic for ARC of SiO.

Fig. 8. Electrical characteristic of the cell for different illumination intensities of incident light for ARC of SiO.

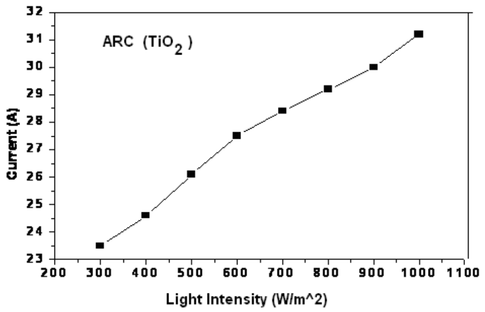
The current voltage characteristics of the devices were measured under illumination for different illumination intensities (from 30 mWcm^{-2} into 85 mWcm^{-2}). The result of samples are shown in Fig. 8 (a). The current in a device is almost directly proportional to light intensity shown in Fig. 8(b).

The short circuit current (I_{sc}) of the solar cells increase with ARC (SiO), and gives the value 26.05 % enhancement in the short circuit current for the specimen.

Fig. 9(a & b) shows that the current voltage characteristics of the devices were measured under illumination for different ilumination intensities (from 300 Wcm^{-2} into 900 Wcm^{-2}), and the current in a device is almost directly proportional to light intensity.



(a) Current-Voltage characteristic of the cell for different illumination intensities of incident light for ARC of TiO_2.



(b) Current-intensity characteristic for ARC of TiO_2

Fig. 9. Electrical characteristic of the cell for different illumination intensities of incident light for ARC of TiO_2.

6. Conclusion

It has been demonstrated that silicon oxide antireflection coating can be used to improve short circuit current in etching of silicon solar cells. The improvement in Isc in solar cells further confirms that the etching of surface passivates. The use of the evaporation, for the deposition of an antireflection coating of SiO on silicon solar cells, proved to be the deposit effect of the characteristic of the deposition technique and of the nature of the silicon surface. The use of the chemical spray technique, for the deposition of an antireflection coating of TiO_2 on silicon solar cells, proved to be the deposit effect of the characteristic of the deposition technique and of the nature of the silicon surface.

The integrated reflectance of the (ARC) structure was reducing to about the same level of the reflectance obtained using antireflection coating deposition by conventional techniques.

Silicon oxide (SiO) and titanium oxide (TiO_2) coatings have been used to reduce the reflection losses from silicon solar cells. 20.6% enhancement in the short circuit current has been demonstrated in the polished cells using evaporated SiO antireflection coating. More than 12% enhancement in the short circuit current has been observed after TiO_2 antireflection coating. The output current is found almost directly proportional to light intensity.

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Appendix

Table 1. Preparation condition of the cold metallization procedure

Sample	Surface cleaning	Process	Metal
M16	None	Etch away	Al (200nm)
M17	Kern (NH_4OH:H_2O_2+HCL: H_2O_2) Boiling H_2SO_4 + $(NH_4)_2S_2O_8$ Boiling HNO_3	Lift off	Al (200nm)
M20	Boling H_2SO_4 + $(NH_4)_2S_2O_8$	Lift off	Al (200nm) Cr(2nm)/Cu(200nm)