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CHARACTERIZATION OF PLAIN AND BORON INTERFACE METAL/p-Si SOLAR CELLS OBTAINED BY SPUTTER METHOD

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SPUTTER YÖNTEMİYLE ELDE EDİLEN SADE VE BOR ARAYÜZEYLİ METAL/p-Si GÜNEŞ PİLLERİNİN KARAKTERİZASYONU

ABSTRACT

In this study, 1.167 mg/ml was prepared with Boric acid in deionized water. Using this solution, Boron coating was made on a molybdenum foil by electrochemical coating method and this coating was confirmed with SEM images. Then, the Si wafer made of p-type ohmic contact with a carrier density of 10^{14} to 10^{18} (1,0,0) orientation was divided into two and this solution was coated on one of them by electrochemical method.

The sample without interface and the sample electrochemical B coated and annealed at 500^0C for 3 minutes were deposited with a 5mm diameter Al magnetron DC sputter method, and a 1mm diameter Au was coated in the middle of it by the evaporation method. As a result of the characterization, for the Au/Al/p-Si/Al/Au structure of the sample without interface; Open circuit voltage (Voc) value is 360 mV, short circuit current (Isc) value is 1130 μA, maximum power (**Pm**) value is 117 (μW), fill factor (FF) value is % 28,68 and conversion efficiency it was observed that the conversion efficiency (η) value was % 0.584.

On the other hand for Au/Al/B/p-Si/ Al/Au structure measurement, related to Au/Al/p-Si/Al/Au structure; while Voc value decreases to 300mV Isc value increased becoming 1570 μA. However, while the Pm value was 118 μW and an increase was observed, a decrease was observed in the FF value and was observed to be % 25,21, and a small increase was observed in the η value and it was observed to be % 0.592.

Keywords: Solar Cell, Sputter Methot, Elektrochemical Coating Methot, Boron, p-Type Silicon

ÖZET

Bu çalışmada, hazırlanan 1,167 mg/ml deiyonize su ile Borik asit ile hazırlandı. Bu çözelti kullanılarak elektrokimyasal kaplama yöntemiyle molibden bir folyo üzerine Bor kaplaması

yapıldı ve bu kaplama sem görüntüleri ile teyit edildi. Sonra 10^{14} ila 10^{18} taşıyıcı yoğunluğuna (1,0,0) yönelimine sahip p tipi omik kontağı yapılmış Silisyum wafer ikiye bölünerek birinin üzerine bu çözelti elektrokimyasal yöntemle kaplandı.

Ara yüzeysiz numune ve elektrokimyasal B kaplanıp 500^0C'de 3 dakika tavlanan numune üzerine 5mm çapına Al magnetron DC sputter yöntemiyle kaplandı ve bunun ortasına 1mm çapında Au buharlaştırma yöntemiyle kaplandı. Karakterizasyon sonucu arayüzeysiz numunenin Au/Al/p-Si/Al/Au yapısı için; Açık devre gerilimi ($\mathbf{V_{ad}}$) değeri 360 **mV**, kısa devre akımı ($\mathbf{I_{kd}}$) değeri 1130 **μA** , maksimum güç ($\mathbf{P_m}$) değeri 117 (**μW**), fill faktörü(**FF**) değeri % 28,68 ve dönüşüm verimliliği(η) değeri % 0,584 olduğu gözlendi.

Öte yandan; ara yüzeyli Au/Al/B/p-Si/ Al/Au yapısı Au/Al/p-Si/Al/Au yapısından alınan ölçümlerle kıyasla $\mathbf{V_{ad}}$ değeri düşüş gösterip 300 **mV** olurken $\mathbf{I_{kd}}$ değeri 1570 **μA** olup artışı gözlendi. Bununla birlikte $\mathbf{P_m}$ değeri 118 **μW** olup artışı gözlenirken **FF** değerinde düşüş olduğu gözlenip % 25,21 olduğu gözlendi ve η değerinde küçükte olsa bir miktarda artış olduğu gözlenip % 0,592 değerinde olduğu gözlendi.

Anahtar Kelimeler: Güneş Pilleri, Sputter Yöntemi, Elektrokimyasal Kaplama Yöntemi, Bor, p-Tipi Silisyum

This article is extracted from my master thesis entitled "characterizatıon of metal / p-si solar cells with organic interfaces wıth pure and boron additives obtined by sputter method" supervised by Kadir EJDERHA (Master's Thesis, Bingol University, Bingöl Türkiye, 2019).

1. INTRODUCTION

The increasing human population in the world and the development of technology due to people's addiction to comfort have resulted to requirement for energy along with comfort. This necessity pushed people to search for energy sources and fossil fuels, a major phenomenon of the last century, were discovered. However, with the increase in the use of fossil fuels, the limited amount of them underground and the vital problem of air pollution and disruption of the natural balance have emerged. Searching for alternative sources to meet energy needs is something that has been on the agenda for a long time. And sunlight, which does not contain any ash and smoke and has played an important role in providing the most basic energy of living things throughout the history of life on Earth, has become a door of hope for scientists in this field as well. Recently, efforts to utilize solar energy have increased significantly.

Semiconductor solar cells have recently become a serious research area. When it comes to semiconductor solar cells; These studies are grouped under the main heading of p-n junction and Schottky junction solar cells, but both of these structures are single, poly, heterojunction and amorphous crystalline solar cells [6]. While all of these structures may be organic, there are also those made with only one side organic or an organic interface. There are studies on the organic interface to increase the rectifying feature, especially for the Schottky structure. In addition, the functioning of a solar cell as a good electricity generator depends on it also being a good rectifier contact [9].

2.1. Monocrystalline Silicon Solar Cells

Silicon (Si); It is a semiconductor material that has been studied extensively and is used in every field, which we encounter in daily life thanks to its electronic capabilities[5].

Within the to begin with commercial sun oriented cells, single gem silicon developed by precious stone drawing strategy was utilized. In this technique, which is still the foremost utilized strategy within the photovoltaic industry, immaculate silicon is gotten by to begin with passing silicon oxide through different chemical and warm responses in circular segment furnaces. Then, a single gem silicon piece called the center is drenched within the silicon soften. When this core is evacuated from the liquefy, the cooled silicon dissolve is kept on the center within the shape of ingots. As before long as this silicon ingot shapes, it is cut into cuts with a chisel. This happens in two stages. To begin with, the ingot is cut into rectangular pieces. These squares are at that point isolated into cuts and prepared into batteries. Their efficiency is around 15%. The disadvantage of these batteries is that they lose a lot of material during construction. They are produced with a thickness of approximately 0.5 mm. Its color is dark blue and its weight is less than 10 grams [3].

2.2. Advantages:

They are made of high-grade silicon and therefore monocrystalline can achieve the highest efficiency rates. Monocrystalline solar panels efficiency rates are generally 15-20%. Monocrystalline silicon solar panels are called space efficient. Monocrystalline solar panels can provide more production with less sun. The proportions of current and volt values are different.

Monocrystalline solar panels are long-lasting. There are currently 50-year-old panels operating in Germany (reference year = 2014). Most solar panel manufacturers offer a 25-year warranty on Monocrystalline solar panels. It tends to perform better in low light conditions than similarly rated polycrystalline solar panels.

3. LITERATURE SURVEY

Zafer [14] with different features; examined photoactive dyes in four main classes: perylenemonoimides (PDI), perylenemonoimides (PMI), perylenemonoanhydrides (PMA) and ruthenium bipyridyl complexes. He also examined three classes of solar cells: organic dye-based nano-crystal structure TiO_2 solar cells (OGP), solid state organic dye-based nano-crystal structure TiO_2 solar cells (Solid State OGP) and organic solar cells (plastic solar cells). Among the dyes, perylenemonoimides (PMI) and perylenemonoanhydrides (PMA) were found to be more suitable for OGP and Solid State OGPs than perylenemonoimides. Perylenediimides (PDI) have been evaluated to be more suitable for plastic solar cells.

Tekerek [11] reported urmberry (morus nigra), black raspberry (rubus idaeus), blackberry (rubus fruticosus), African okra (hibiscus sabdariffa l.), purple carrot (daucuscarota l.) and mixture (raspberry, urmuberry, blackberry mixture) was used. Current-Voltage (I-V) characteristics of the batteries were carried out in a clear sunny weather between 12:00-13:00 in June-July, and calculated the efficiency of bmgp with the help of the figure obtained from I-V measurements, and obtained the efficiency as (η = 0.248%) in the sample in which carrots were used.

Sandıkçı [8] used elements boron, selenium and lead, which are commonly used as additives in the production of semiconductor alloys, and studied the effect of these additives on the properties of the produced semiconductor alloys. In the experimental study, Sb2Te3 and Bi_2Te_3 alloy samples prepared with different stoichiometric ratios and different additives were vacuum sealed in quartz tubes and melted in a rotary kiln. He placed the samples removed from the tube furnace in a crystal growth system to produce the semiconductor alloys. Structural and thermal analysis of the samples prepared after synthesis were performed using X-ray diffraction (XRD), scanning electron microscope (SEM) and differential thermal analysis-thermogravimetry (DTA-TG) instruments. As part of his research, he prepared alloys of [75% Sb_2Te_3 + 25% Bi_2Te_3] and [75% Sb_2Te_3 + 25% Bi_2Te_3 + %Te] and added 1%, 3% and 5% B-, Se- and Pb to these. He used these alloy additives and investigated their structural properties.

Orak et al. [4] investigated the coating thickness, current-voltage (I-V) and capacitance-voltage (C-V) characteristics of Al/Azure C/p-Si heterojunction layers prepared using a spin-coating system under room temperature illumination conditions. From current-voltage measurements with thermionic emission current equation, they found several heterojunction parameters such as ideality factor and barrier height at 1.10, 1.15, 1.26 and 0.57 eV for undoped, 2 ml/cm2 and 4 ml/cm2, respectively. They obtained 64 eV and 0.65 eV. They stated that as the organic layer thickness increases, the ideality factor, barrier height and photovoltaic power increase and the device capacitance decreases.

Niripendra et al. [7] in their paper found that in Schottky solar cells, the barrier height plays a key role in determining various cell parameters. Chemical vapor deposition was observed to vary the Schottky barrier height by growing metalorganic quantum dots in milk on p-Si. The barrier height was found to be dependent on the size and shape of the nanostructures. A sample with a barrier height of 0.71 eV, open circuit voltage of 0.51 V, and short circuit current density of 13.29 mA/cm2 under 1.5 hours of standard sunlight was found to have a conversion efficiency of 3.89%. The sample prepared to vary the barrier height of the nanostructures showed an increase of 2.82% compared to the reference sample.

4.MATHERIAL and METHOD

4.1. BORON

Elemental boron was first discovered in 1808 by the French chemist Gay-Lussac and Baron Louis Thenard, and independently by the English chemist Sir Humpry Davy. Boron is an element with the symbol B in the periodic table, with atomic number 5, atomic mass of 10.8 g, density of 2.84 g/cm^3, melting point of 2200°C and boiling point of 3660°C, and has semiconductor properties between metal and nonmetal [16]. Boron crystal is the hardest element after diamond [10].

When boron is added to the molten glass intermediate product, it increases its viscosity and increases the surface hardness and particles. In the glass industry, it is added to glass products where heat insulation is required; The perspective of the ceramic industry is that enamel coated with boron prevents it from rusting and makes ceramics resistant to scratches; In soaps and detergents, for cleaning and whitening due to its antimicrobial, water softening and whitening effects; In the construction and cement industry, as it increases durability and provides insulation properties; since it’s melting point is very high and therefore it is quite resistant to burning, it is used as a fire retarder/preventer; Due to the very high neutron absorption power of boron, it is used in nuclear applications; In hydrogen production and storage, as engine fuel, as engine fuel additive in the energy sector; Boron minerals are used in agriculture in order to increase or prevent the development of vegetation; Due to boron chemicals' ability to form a smooth, sticky, protective and clean liquid at high temperatures, they are used in machinery and metallurgy as a protective slag former, melting accelerator and especially steel hardness increasing agent. BNCT (Boron Neutron Capture Therapy) is used in cancer treatment.

Especially; It is used to selectively destroy diseased cells in the treatment of brain cancers and is used in the healthcare industry because its damage to healthy cells is minimal [13]. And also Boron is widely used in silicon-centered p-type dopant semiconductor technology [15]. Boron and boron compounds in silicon structures have an important place in material science and semiconductor technology [5]

Boron mines, described as the oil of the 21st century, are Turkey's only strategically important mineral asset. Boron minerals, which have no substitutes, are used in a wide range of areas, from space technology to the energy sector, from nuclear technology to the defense industry [13]. For this reason, many researchers continue their studies to discover new areas of use of boron and its compounds or to observe the different effects of boron on existing areas of use with new methods.

4.2. Photovoltaic Principle of Metal/p Type Si

Let's consider a metal-semiconductor contact whose energy band diagram is given in Figure 4.1. And let a load resistor be connected to this joint. Even at zero voltage supply, there is an electric field at the junction of this joint, called the space charge region, which occurs due to the obstacle height. And if the sunlight falling here has enough energy, it creates an electron-hole pair. The electric field here sweeps this pair out and creates a photopotential. A current IL occurs in the opposite direction of the resistor diode connected to the circuit. [9]

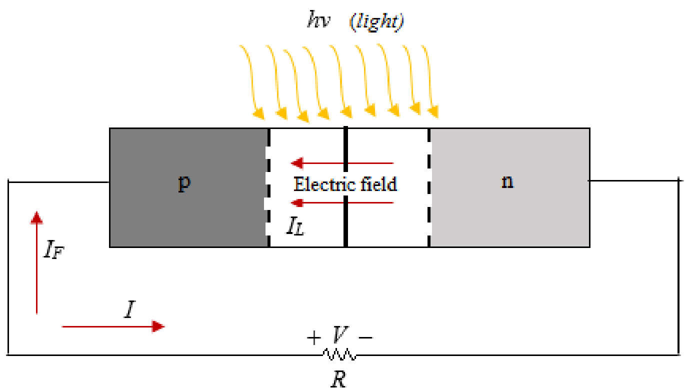


Figure 4.1.: A p-n junction solar cell with a resistive load [6]

This I_L current results a potential on the load resistor, and this potential is reflected to the diode as a direct supply and some of the produced current is discharged through the diode. Expressing this;

Inet = I_L-I_F (4.1)

In the equation; Inet is the net current, IL is the Photocurrent and IF is the direct supply current of the diode. The straight supply current equation for the ideal diode is given in Equation 1. If the diode is fed straight, the electric field value in the space charge region decreases, but there is never zero or reverse rotation. Therefore, the photocurrent is always in the opposite direction and the net current is in this direction [6].

Some parameters can be found by examining two limit conditions. For example, if R = 0, V = 0 and the net current passing here is called short circuit current.

And

$$I_{net} = I_{sc} = I_L \tag{4.2}$$

I_{sc} is the short circuit current. On the other hand, in the case of $R \to \infty$;

$$I_{net} = 0 = I_L - I_0\left[\exp\left(\frac{eV_{oc}}{kT}\right) - 1\right] \tag{4.3}$$

obtained. In other words, since no current flows, the circuit behaves like an open circuit and the open circuit voltage Vad is obtained here and the open circuit voltage can be found as follows.

$$V_{oc} = V_t \ln\left(1 + \frac{I_L}{I_0}\right) \tag{4.4}$$

Here Vt = e/kT is the thermal potential. Power reaching load resistance, it is written as;

$$P = I.V = I_L.V - I_0\left[\exp\left(\frac{eV}{kT}\right) - 1\right].V \tag{4.5}$$

If the derivative is taken with respect to I, the voltage point at the maximum power reaching the load resistance is obtained at the point where dP / dV = 0.

$$\frac{dP}{dV} = 0 = I_L - I_0\left[\exp\left(\frac{eV_m}{kT}\right) - 1\right] - I_0 V_m\left(\frac{e}{kT}\right)\exp\left(\frac{eV_m}{kT}\right) \tag{4.6}$$

Using equation (5.2.3.4), the maximum voltage value Vm can be obtained by valuation.

$$1 + \left(\frac{V_m}{V_t}\right)\exp\left(\frac{eV_m}{kT}\right) = 1 + \frac{I_L}{I_0} \tag{4.7}$$

A metal-semiconductor or p-n junction solar cell is a device that converts the energy of photons into electrical energy. The maximum efficiency of a silicon p-n junction solar cell is about 28%. For a solar cell, the conversion efficiency is defined as the ratio of the power delivered to the optical power consumed. For the maximum value of the power, the following equation can be written [6]:

$$\eta = \frac{P_m}{P} \times 100\% = \frac{I_m V_m}{P} \times 100\% \tag{4.8}$$

Now a parameter called fill factor can be defined. [1]

$$F_F = \frac{I_m V_m}{I_{sc} V_{oc}} \tag{4.9}$$

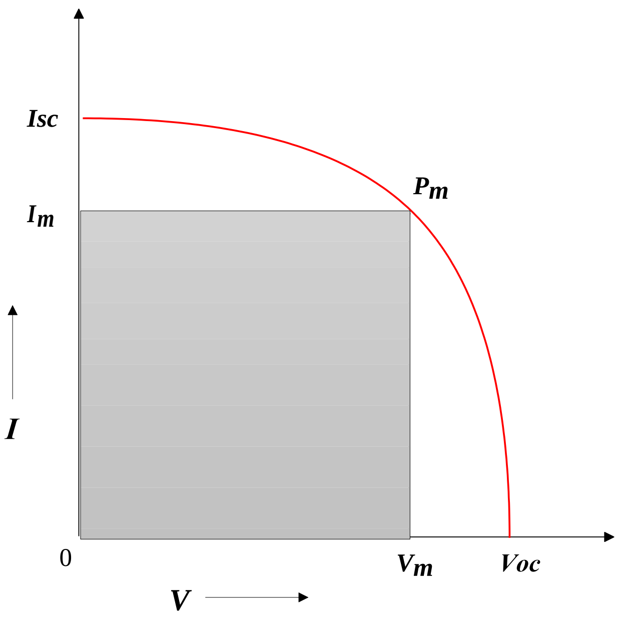


Figure 4.2.: Maximum power rectangle of solar cell I-V characteristic [6]

The highest possible current and highest possible voltage of the solar cell are I_{sc} and V_{oc} respectively. The $I_m V_m / I_{sc} V_{oc}$ Ratio is a measure of the power that can be realized in a solar cell, called the fill factor. Fill factor is the ratio of the current and voltage value at the maximum power value and the area of the rectangle formed by the open circuit voltage and closed circuit current. The fact that this ratio is small is related to the homogeneity of the barrier height of a rectifier contact. Typically, the fill factor is between 0.7 and 0.8. [6]

Since a thin oxide layer of 5–20 Å thickness naturally forms between the metal and semiconductor, the equation should be corrected as follows: [2]

$$I = I_0 \left[\exp\left(\frac{eV}{nkT}\right) - 1\right] \qquad (4.10)$$

Here n is the ideality factor. If the logarithm of both sides of the equation is taken and the derivative is taken with respect to V,

$$n = \frac{e}{kT}\frac{dV}{d(lnI)} \qquad (4.11)$$

equality is obtained.

5. RESULTS

Since the study was to be carried out on Si wafers, firstly a p-type substrate with a carrier density of 10^{14} to 10^{18} (1,0,0) orientation was obtained and then, according to the Si cleaning procedure, it was washed ultrasonically, first in acetone and then in methanol for 10 minutes each. Then, it was washed thoroughly with 18.3 Mohm resistivity deionized water (DIW). Then, it was washed in RCA1 (H_2O:H_2O_2:NH_3;6:1:1) at 60 °C for ten minutes. Then, it was washed with dilute HF (H_2O;HF;10:1) for 30 seconds. Then, it was boiled in RCA2 (H_2O:H_2O_2:HCl;6:1:1) at 60 °C for 10 s. Then it was washed thoroughly with DIW. Then, it was washed with dilute

HF (H_2O;HF;10:1) for 30 seconds. Then, it was placed in running deionized water for 15-20 minutes and then dried by spraying pressurized N_2 inert gas. An ohmic contact had to be made on the matte side of the sample. For this purpose, the heater was first washed with 10% HCl, thoroughly washed with deionized water, dried, and then placed in the vacuum device and burned and made ready. Then, the 99.98% purity aluminum (Al) ohmic contact metal to be evaporated was chemically cleaned and placed on the heater, and thermal cleaning was carried out by pre-melting. Immediately afterwards, our Si substrate was placed with the matte side facing the heater, that is, the bottom, and the system vacuuming procedure was started. After waiting for the system to drop to ~10^{-7} torr pressure, current was applied to the heater and the ohmic contact metal boiled and evaporated and was coated on the substrate (~100nm thick). Meanwhile, the amount of the coated material was determined with a quartz thickness sensor.

After waiting for a while, air was introduced into the vacuum device, the sample was removed from the vacuum device, placed in a chemically cleaned quartz crucible, and annealed for 3 minutes in the oven previously lit and set at 585oC. Then, a thin layer of gold (Au) was coated on it to prevent Al oxidation. Thus, the ohmic contact process is completed.

To prepare the boric acid solution containing boron compound as an interface, certain proportions of boric acid compound were mixed with DIW at a ratio of 1.167/1 mg/ml. Using this solution, boron coating was made on molybdenum foil by electrochemical coating method. It was then analyzed in XRD. The ohmic contact Si was divided into two parts; One part was separated as the reference sample and the other as the interfaced sample. Boron coating was made by taking interfaced p-Si and using the electrochemical coating method.

Then, to perform the rectifier contact process, coated or uncoated substrates were placed on the NVTS 400 device prepared for Al Sputter and covered with a light-transmitting Al layer with a diameter of 5 mm and a thickness of approximately 10 nm. Then, to make contact, 1 mm diameter and 100 nm thick Au was coated on one side of the Al layer by evaporation method. Then, after waiting for a while for the substrate to cool, air was introduced into the system and the substrates were removed. The prepared Au/Al/p-Si/B/Al/Au and reference structure were taken into the point contact measurement system for measurement and characterization of these cells was done with the help of Keithley 2400 and Coınc-16s-150-002 solar simulator and a labview control program at 25 ^{O}C room temperature. and 100 mW/cm^2 (Figure 5.1 and Figure 5.2.) sunlight power was performed in a laboratory environment.

Then, in the characterized samples, fill factor, conversion efficiency, short circuit current, open circuit voltage and maximum power values were calculated from measurements in the point contact measurement system.

As it is known, when H_3BO_3 dissolved in water reacts with water, the $H_2BO_3^-$ compound containing hydronium (H_3O^+) ion and Boron is in solution. Since the Mo foil is bound to the cathode part in the electrochemical coating process, this B compound will stick to the Mo foil and the H and O ions in it will evaporate with annealing. Some layer B will remain on the surface. [12] reported that he synthesized MoB compound under 600 ^{0}C temperature in his experiment.

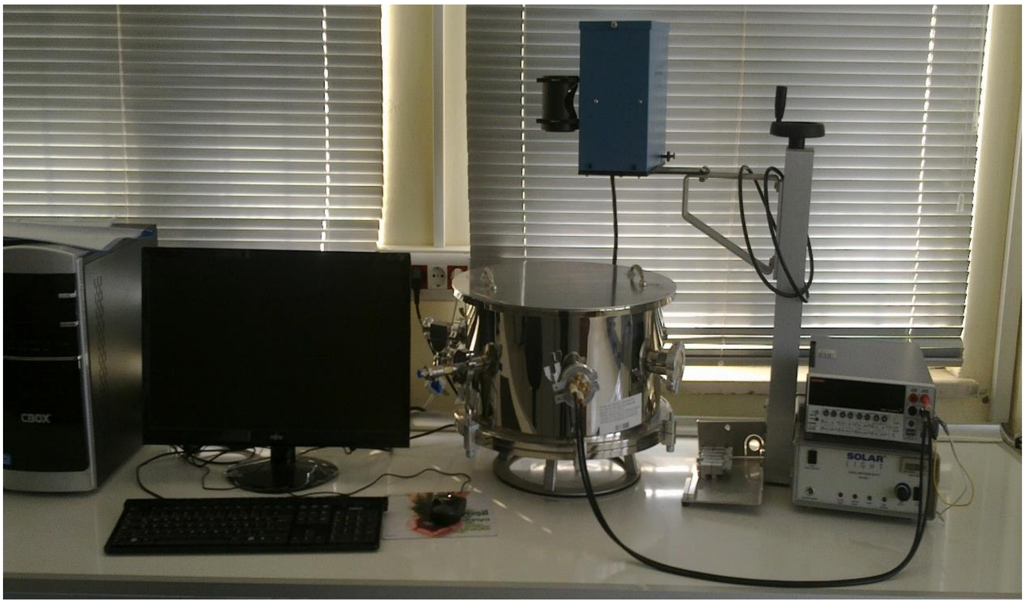
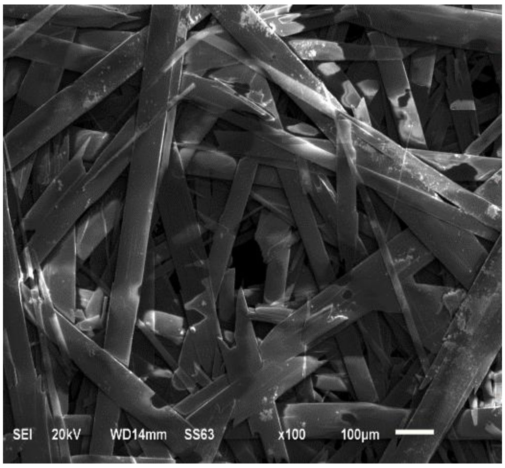


Figure.5.1.: Point contact measurement system in the laboratory environment where measurements are taken

Figure 5.2.: If the SEM images are examined, it can be seen that the wire-shaped surface of the plain molybdenum foil, which is 100 µm long, is covered with a Boron layer for 120 minutes by electrochemical method with a 1.167 mg/ml solution prepared, and even the 5 µm-long Boron particles are in a close to regular arrangement and wire-shaped. It can be seen that the surface is covered.

a) 

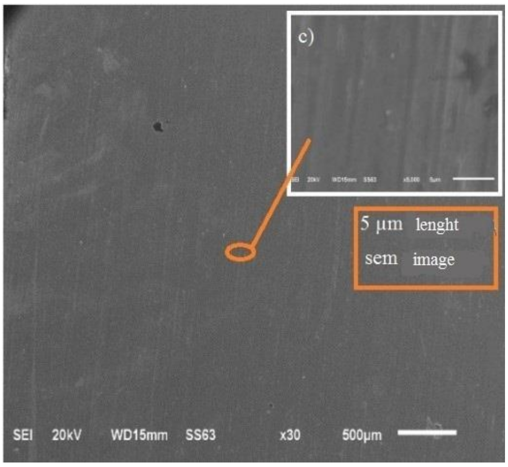
b) 

Figure 5.2.: SEM images of Mo Foil subjected to different processes.
a) Plain Mo foil 100 µm b) Electrochemical B coated (120min) Mo foil (5µm)

The graphics of the structure without interface are given in Figure 5.3, and the graphics of the sample with interface are given in Figure 5.4. While the interface sample was being prepared, it was subjected to electrochemical treatment for two hours with previously prepared Boric acid solution. Then, Al was coated on the front of both samples in a circular shape with a diameter of 5 mm and a thickness of 7 nm using the sputter technique, and measurements were taken in the point contact measurement system.

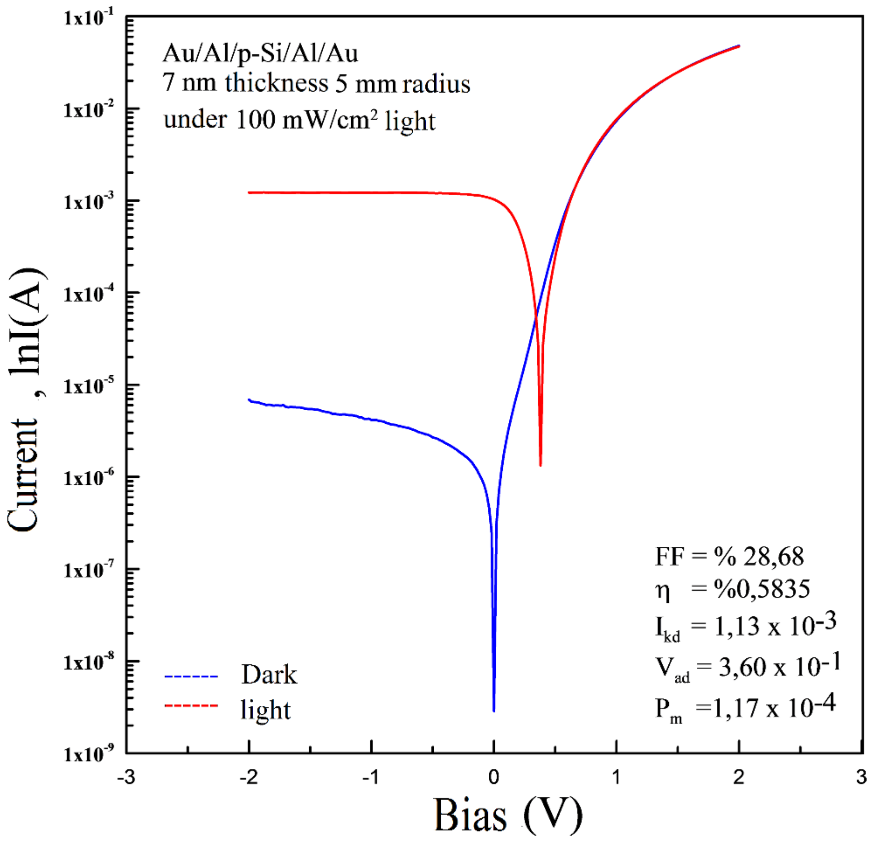


Figure 5.3.: Current-Bias graph of the Au/Al/p-Si/Al/Au structure.

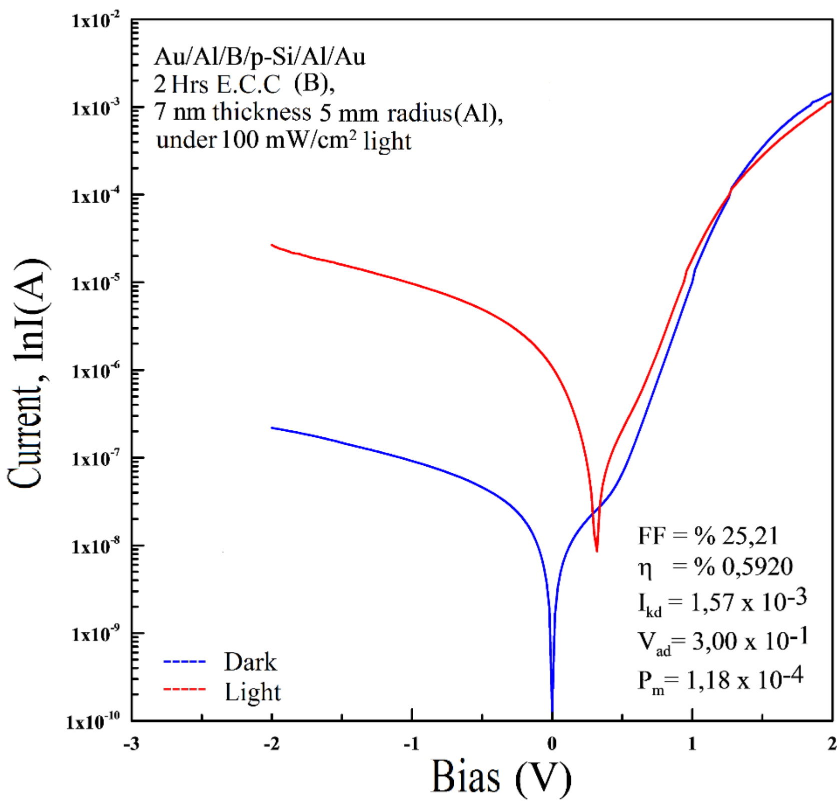


Figure 5.4.: Current-Bias graph of the Au/Al/B/p-Si/Al/Au structure

6. DISCUSSION

In the study, the non-interfaced sample Au/Al/p-Si/Al/Au structure was characterized. And it was observed as the open circuit voltage (**Voc**) value is 360 mV, short circuit current (Isc) value is 1130 **μA**, maximum power (Pm) value is 117 (**μW**), fill factor (FF) value is % 28,68 and the conversion efficiency (**η**) % 0.584.

Likewise, the Au/Al/B/p-Si/Al/Au structure with B interface was also characterized. According to the measurements taken after Boron coating with the electrochemical coating method for 2 hours, then annealing at 500 ^{o}C for 5 minutes and coating with the Sputter technique, the V_{oc} value decreased and became 300 mV, while the Isc value decreased compared to the measurements taken from the Au/Al/p-Si/Al/Au structure in the 1st group. 1570 **μA** and an increase was observed. However, while the Pm value was 118 **μW** and an increase was observed, a decrease was observed in the FF value and was observed to be % 25,21, and a small increase was observed in the **η** value and it was observed to be % 0.592.

7. CONCLUSION

In our research, it was observed that a boron layer was coated on a molybdenum foil by electrochemical coating method from water-soluble boric acid. In this context, improvements in the parameters were observed, albeit slightly, in the sample with B coating. For example, while V_{oc} and I_{sc} values decrease at the interfaced B; Increases were observed in **Pm** and **η** values. On the other hand, as seen in the SEM images, B coating on Mo foil was successful. On the other hand, it has been reported that MoB compound was synthesized by annealing at 600 degrees [12]. In this context, considering the chemical cycle, it can be said that B is coated on the interface, considering the temperature of 500 degrees, which is close to 600 degrees. As a result, the interface B layer contributed slightly to the solar cell measurements.

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