

Characterization of CuO/n-Si heterojunction solar cells produced by thermal evaporation

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Copper(II) oxide (CuO) in powder form was evaporated thermally on the front surface of an n-Si (1 0 0) single crystal using a vacuum coating unit. Structural investigation of the deposited CuO film was made using X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) techniques. It was determined from the obtained results that the copper oxide films exhibited single-phase CuO properties in a monoclinic crystal structure. Transmittance measurement of the CuO film was performed by a UV-Vis spectrophotometer. Band gap energy of the film was determined as 1.74 eV under indirect band gap assumption. Current-voltage (I-V) measurements of the CuO/n-Si heterojunctions were performed under illumination and in the dark to reveal the photovoltaic and electrical properties of the produced samples. From the I-V measurements, it was revealed that the CuO/n-Si heterojunctions produced by thermal evaporation exhibit excellent rectifying properties in dark and photovoltaic properties under illumination. Conversion efficiencies of the CuO/n-Si solar cells are comparable to those of CuO/n-Si produced by other methods described in the literature.

Keywords: *copper oxide; heterojunction; photovoltaics; solar cell; rectifier*

1. Introduction

Copper oxide has several advantages in the photovoltaic production. These are low production cost, non-toxicity and high optical absorption. Apart from these, the basic two phases of copper oxide i.e. monoclinic cupric oxide (CuO) and cubic cuprous oxide (Cu₂O) are natural p-type semiconductors and their energy band gap values are 1.2 eV to 1.9 eV and 1.8 eV to 2.5 eV, respectively; these values are suitable for photovoltaic applications. Due to these advantages, copper oxide attracted great interest of the researchers [1–9]. However, this binary system may contain also other oxides, such as Cu₃O₂ or Cu₄O₃ (paramelaconite). It was reported that paramelaconite (Cu₄O₃) has values of 2.47 and 1.34 eV for direct and indirect band gap, respectively [10, 11].

It was reported that copper oxide films (Cu_xO) produced by thermal evaporation technique and characterized morphologically using X-ray diffraction spectra, are amorphous [12]. In another study, copper oxide films were deposited by thermal evaporation of Cu₂O powder on a substrate, either unheated or heated and some of them were subjected to annealing. As a result of the investigation, it was reported that the films consisted of mixed CuO, Cu₂O phases, and CuO phase was dominant depending on the substrate temperature and annealing [13]. The film deposited by vacuum thermal evaporation using Cu₂O powder was examined. It was determined that the film consisted partially of Cu (1 1 1) crystal phase and the dominant amorphous phase. However, when this film was subjected to thermal annealing in air, it was reported that a p-type Cu₂O film was formed [14].

In the copper oxide film deposition process, temperature is one of the most important factors

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for phase formation of the films. If the substrate temperature is too low, the resulting copper oxide film is mostly amorphous. If the substrate temperature is around 250 °C to 300 °C, the film predominantly occurs in Cu₂O phase. If the temperature is over 300 °C, especially around 450 °C to 500 °C, the film predominantly occurs in the CuO phase. Copper oxide films may crystallize in more than one phase, that is the films may consist of a mixture of the phases. At the lowest temperature, amorphous film predominates, as the temperature increases, Cu₂O phase dominates and at higher temperatures CuO phase prevails [10–14].

In the production of cupric oxide/n-Si heterojunction solar cells, sputter technique was used. Conversion efficiencies of these cells were reported as around 1 %. Efficiency values for some CuO/n-Si heterojunction solar cells described in the literature ranged from 0.41 % to 1.2 % [1–5]. For CuO/Cu₂O heterojunction solar cell, efficiency of 0.64 % has been achieved [6], for AZO/n-oxide semiconductor/p-Cu₂O and for AZO/Ga₂O₃/Cu₂O heterojunction solar cells efficiencies of 5.38 % were reported [7, 8].

In this context, we have attempted to use thermal evaporation method, never used before in the production of CuO/n-Si heterojunction solar cells. We deposited CuO powder on the front surface of n-Si (1 0 0) wafer by thermal evaporation using a vacuum coating unit. We obtained the conversion efficiency values comparable to those of the CuO/n-Si heterojunction solar cells produced before by various methods.

2. Experimental

A n-type Si wafer with (1 0 0) orientation and resistivity of 1 Ω·cm to 10 Ω·cm was used to fabricate CuO/n-Si heterojunction solar cells. The wafer was chemically cleaned using a standard RCA procedure (i.e. the wafer was boiled in the solution of NH₄ + H₂O₂ + 6H₂O for 10 min, then boiled in the solution of HCl + H₂O₂ + 6H₂O for 10 min and etched in dilute HF:H₂O (1:10) for 30 s to remove the native oxide layer on the surface. Between the process steps, the wafer was

washed in deionized water with a resistivity of 18 MΩ. The chemically cleaned wafer was dried under N₂ gas and inserted into a vacuum coating unit for metallization. The ohmic back contact was formed by evaporating Al on the back surface of the substrate, followed by a temperature treatment at 450 °C for 3 min in N₂ gas. CuO powder was evaporated on the front surface of the n-Si wafer, with a film thickness of about 150 nm. In such way, CuO/n-Si heterojunction solar cells were fabricated. Film thickness of the top contact was controlled using a film thickness monitoring system in the vacuum coater unit. EDX and XRD techniques were used for structural studying the copper oxide film while the optical transmittance measurement of the copper oxide film was performed using a UV-Vis spectrophotometer. The electrical properties of the CuO/n-Si heterojunctions were characterized by dark current-voltage (I-V) measurements. Also, their photovoltaic properties were evaluated using the I-V measurements, carried out under an illumination of 100 mW/cm² and AM 1.5.

3. Results and discussion

Production details of CuO/n-Si heterojunction solar cells made by thermal evaporation are given in Section 2. CuO is an intrinsic p-type semiconductor since there may be a spontaneous Cu vacancy formation in the structure [5]. Cupric oxide in powder form as received from the manufacturer was evaporated on the front surface of n-Si, without any further treatment. Thus, a p-CuO/n-Si heterojunction structure was formed.

The CuO/n-Si heterojunction solar cells were studied in terms of electrical, optical, photovoltaic and structural parameters. I-V measurements of the CuO/n-Si structures were taken in dark for studying the electrical characteristics. For determining photovoltaic characteristics of the CuO/n-Si heterojunction solar cells, I-V measurements were performed under illumination. Dark I-V plots and illuminated and dark I-V plots of the copper oxide/n-Si are given in Fig. 1a and Fig. 1b, respectively.

As seen from Fig. 1, CuO/n-Si heterojunctions exhibit rectifying properties. If a contact obeys

simple thermionic emission theory (TE), its forward bias current in I-V graph must show an exponential character. Therefore, we can express the current as [15–18]:

$$I = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right) \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \quad (1)$$

where

$$I_o = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right) \quad (2)$$

is saturation current, Φ_b is barrier height, A^* is Richardson constant equal to $112 \text{ A/cm}^2 \cdot \text{K}^2$ for n type Si, q is electronic charge, V is applied voltage, k is Boltzmann coefficient, T is ambient temperature in K and it was taken as 300 K. In case of $qV > 3kT$, equation 1, is reduced to the following expression:

$$I = I_o \exp\left(\frac{qV}{nkT}\right) \quad (3)$$

where n is ideality factor which is a measure of conformity of diode to pure thermionic emission and is determined from the slope of the straight line region of a forward bias \ln I-V characteristics through the relation:

$$n = \frac{q}{kT} \frac{dV}{d(\ln I)} \quad (4)$$

Ideality factor for a rectifying contact is a measure of whether it is an ideal contact. If ideality factor value for a rectifying contact is equal to 1, it indicates that the contact is ideal. If the value of the ideality factor tends towards the values larger than 1, it indicates that the contact is away from the ideal case.

As can be seen, the values of ideality factor for the CuO/n-Si contacts are considerably larger than 1. Thus, we can deduce that the contacts are not ideal. In fact, it was expected that the contacts would not be ideal because the evaporated material was oxidized.

The values of ideality factor n of the CuO/n-Si contacts were calculated using equation 4 and dark I-V data. As can be seen from Table 1, the values

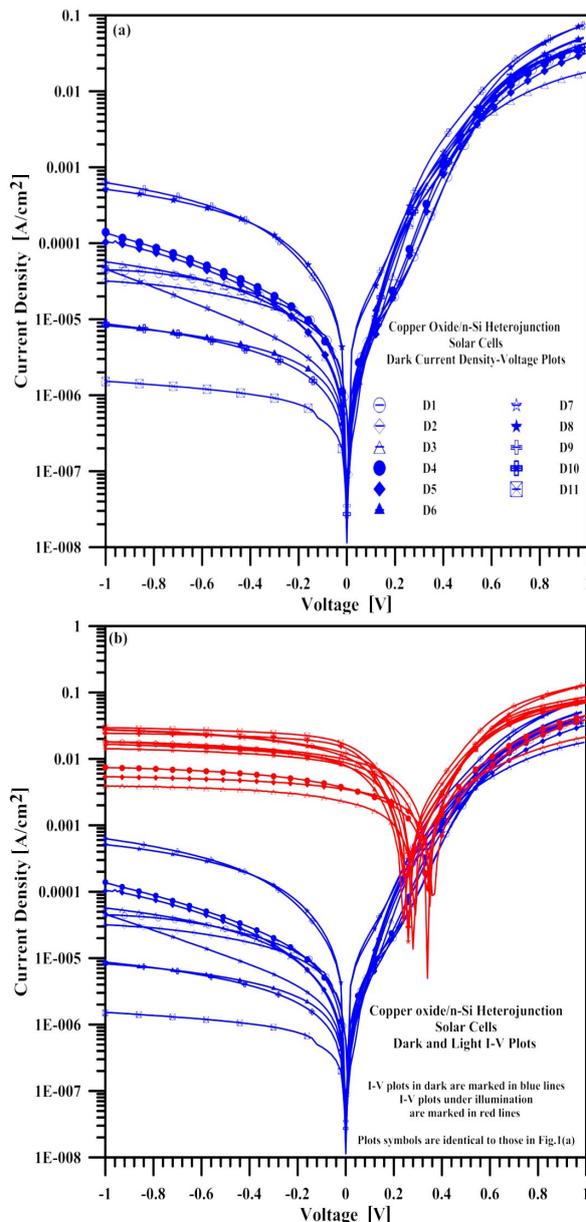


Fig. 1. (a) Dark I-V plots of CuO/n-Si heterojunction solar cells produced by thermal evaporation; (b) dark and illuminated I-V plots of the CuO/n-Si heterojunction solar cells produced by thermal evaporation.

of ideality factor range from 1.82 to 2.88. The values of rectification factor, which is an important indicator of whether the contact is a good rectifier, range from 87.67 (for D9) to 17881.79 (for D11). The values obtained from dark I-V measurements reveal the electrical characteristics of the produced

contacts. It is seen from Fig. 1a and the characteristic values in Table 1 that CuO/n-Si heterojunction structures produced by thermal evaporation have good rectifying properties.

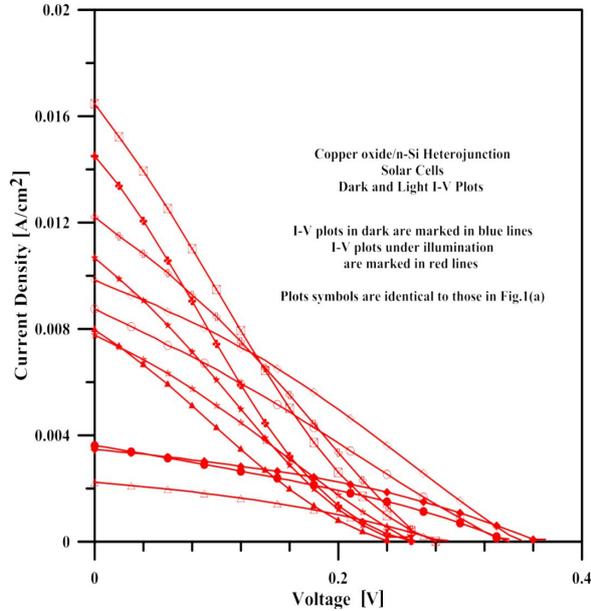


Fig. 2. Photovoltaic characteristics of CuO/n-Si heterojunction solar cells produced by thermal evaporation.

Moreover, it is seen from the curves in both Fig. 1b and Fig. 2, plotted based on the I-V measurements taken under illumination, that the CuO/n-Si heterojunction structure exhibits photovoltaic properties. That is, the CuO/n-Si heterojunction structure exhibits both good rectifying and photovoltaic properties. However, it is known that there is relation between diode and photovoltaic parameters of a p-n junction solar cell. The relationship between rectifying and photovoltaic properties of Sn/p-Si Schottky type photojunction was also discussed in our previous article [19].

Some parameters in the production process may adversely affect the rectifying and photovoltaic properties of CuO/n-Si interface. For example, it is necessary to pay attention to n-Si crystal surface temperature during the deposition of CuO film on the front surface of the crystal in the vacuum coating unit, because the rectifying behavior of the CuO/n-Si interface can be negatively affected

by the contact temperature. Rectifying properties of the n-Si/CuO interface are also important for its photovoltaic characterization.

Table 1. Selected electrical parameters of the CuO/n-Si heterojunction solar cells obtained from dark I-V measurements.

Sample name	Ideality factor n	Rectification factor
D1	2.59	532.77
D2	2.88	827.68
D3	1.82	252.26
D4	2.09	244.15
D5	2.05	225.38
D6	2.40	3923.8
D7	2.11	1093.3
D8	2.50	96.050
D9	2.15	87.670
D10	2.53	3297.6
D11	2.30	17882

To prevent overheating of the crystal surface, the distance between the heater metal and the target crystal must be well adjusted. In addition, evaporation time (coating speed) is also important. Vacuum level, heater metal properties also affect the process.

It is also important that the CuO film, which is deposited on the crystal surface, was homogeneous. For this reason, attention must be paid to the distance between the heater metal and the target crystal, and the coating period. For example, if the distance between the target crystal and the heating metal is too large, the crystal surface is prevented from being heated, but in this case the homogeneity of the film is affected adversely. If the coating process is carried out too slowly, then the film will not be homogeneous and the crystal surface will be more heated.

We kept the n-Si crystal at a distance of about 10 cm from the heater metal, taking into account all the parameters that could affect the rectifying properties of CuO/n-Si interface and CuO film homogeneity.

Another matter for photovoltaic performance of the CuO/n-Si heterojunction is CuO film thickness.

Film thickness in a p-n junction solar cell is an important parameter in terms of photon absorption and solar cell efficiency. An increase in photocurrent is attributed to the improvement of light absorption along with an increase in CuO film thickness. However, the further increase of the CuO thickness (~ 700 nm) causes deterioration of the photocurrent. Thus, the optimum thickness determined for photocurrent is about 550 nm [20].

Photovoltaic features of the CuO/n-Si heterojunctions are seen clearly in Fig. 1b and Fig. 2 which show I-V plots of the samples under illumination. From short circuit current I_{sc} and open circuit voltage V_{oc} of the samples (Fig. 2), fill factor FF value and efficiency η of the devices can be determined using equation 5 and equation 6 [21]:

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (5)$$

where V_m is the maximum voltage and I_m is the maximum current, respectively corresponding to the maximum output power P_{max} . That is $P_{max} = V_m I_m$. V_{oc} and I_{sc} represent open circuit voltage and short circuit current of the samples, respectively. FF is the ratio of the rectangular area formed by multiplication of V_m and I_m to the rectangular area formed by multiplication of V_{oc} and I_{sc} , in a photovoltaic current-voltage graph. Conversion efficiency η is given as follows:

$$\eta = \frac{V_m I_m}{P_{in}} \quad (6)$$

where P_{in} is the photon power incoming to the sample per surface area. Table 2 shows some photovoltaic characteristics of the samples such as V_{oc} , I_{sc} , P_{max} , FF and η . V_{oc} values range from 0.25 eV to 0.35 eV, FF values range from 0.19 to 0.35 and η values range from 0.22 % to 1.00 %.

The highest yield achieved up to now in copper oxide/n-Si heterojunction solar cells is 1.2 %. Our efficiency of 1 % for CuO/n-Si heterojunction solar cells produced by thermal evaporation may seem like a small value, but it is comparable to the values obtained for CuO/n-Si produced before [1–5].

CuO/n-Si heterojunctions described in the literature were produced by two-step sputtering [1],

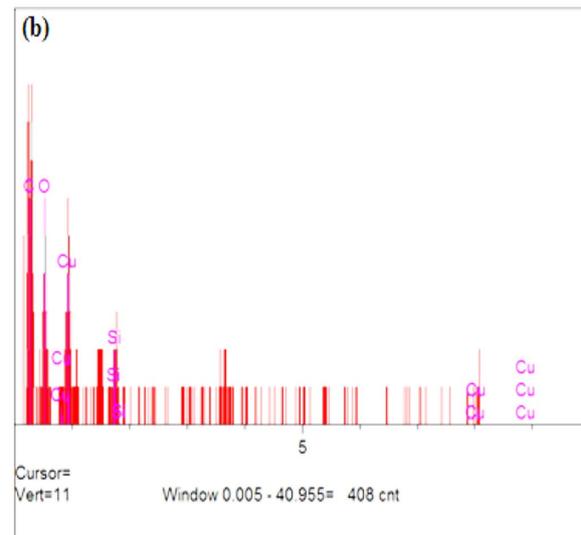
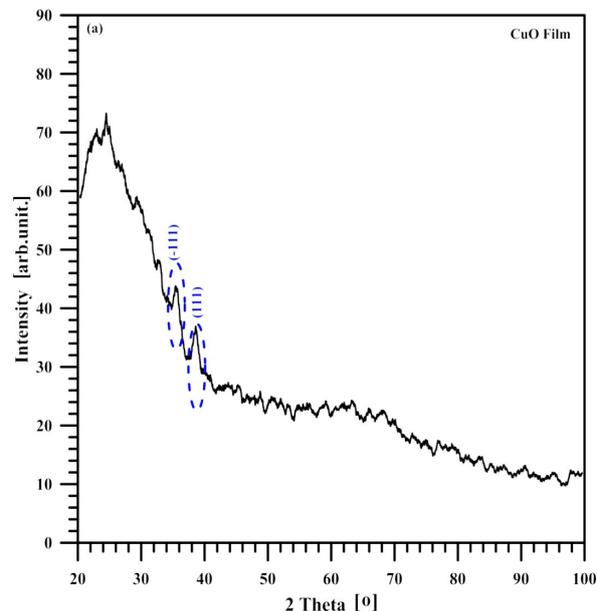


Fig. 3. (a) X-ray diffractogram of CuO film produced by thermal evaporation; (b) energy dispersive X-ray analysis (EDX) of CuO film produced by thermal evaporation.

sputter and rapid thermal annealing [2] and magnetron sputtering [3]. In our study, CuO/n-Si was produced by thermal evaporation.

As can be seen from Fig. 2, which is based on the I-V measurements under illumination, the FF values are quite small. This can be attributed to the contact interface. Because the FF value is related to the curling shape of I-V curve, it can

be seen that the shape of the I-V curve in Fig. 2 directly affects the value of the $V_m I_m$ term in equation 5 and equation 6. On the other hand, in the formation of the I-V shape in a rectifier contact, it is also known that the interface has a dominant effect. This indicates that the fill factor is related to the interface nature of the contact.

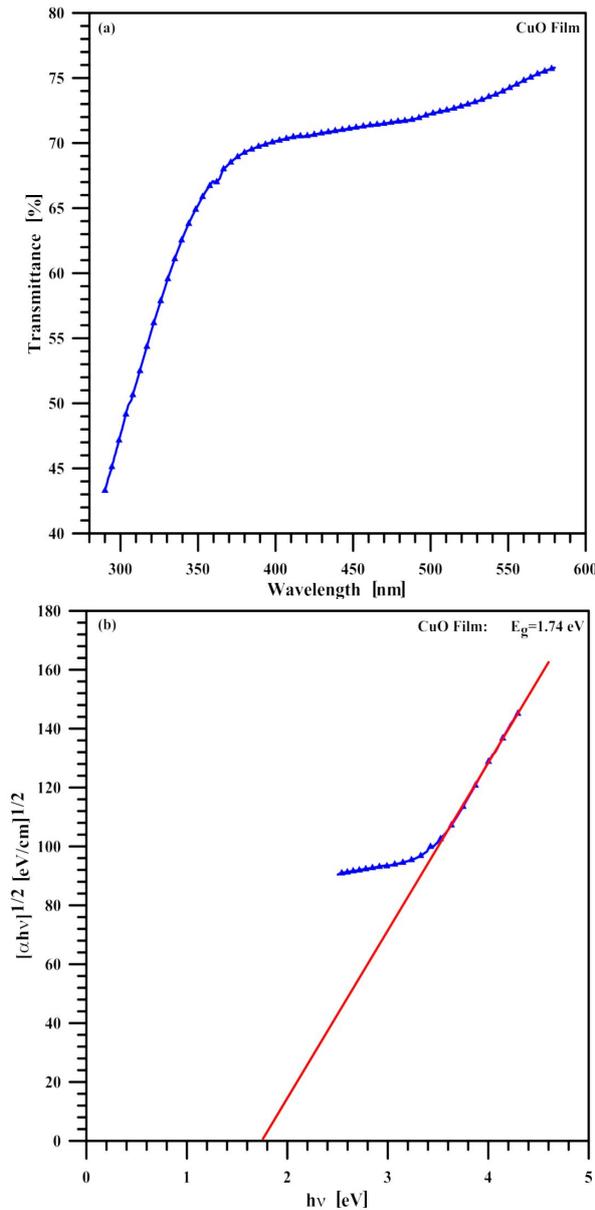


Fig. 4. (a) Transmittance plot versus photon wavelength for CuO film produced by thermal evaporation; (b) plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy $h\nu$ of CuO film produced by thermal evaporation.

As can be seen from Fig. 3a, two weak peaks are observed in the X-ray photoelectron diffraction (XRD) pattern of the copper oxide film produced by thermal evaporation. These peaks located at $2\theta = 35.6^\circ$ and $2\theta = 38.7^\circ$ can be correlated with the $(-1\ 1\ 1)$ and $(1\ 1\ 1)$ crystal planes of monoclinic CuO structure. Fig. 3b exhibits EDX results obtained for the CuO film and shows clearly the presence of copper and oxygen atoms.

A UV-Vis spectrophotometer was used for optical investigation of the CuO film produced by thermal evaporation. Transmittance measurement of the film versus photon wavelength was performed. The sharp drop of the plot in Fig. 4a, indicates the presence of energy band gap of the CuO film. Fig. 4b shows the plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy $h\nu$ of the CuO film produced by thermal evaporation. By extrapolation of the linear portion of the plot to the energy axis, the value of the band gap energy E_g was determined to be $= 1.74$ eV for the CuO film. This value is very suitable for photovoltaic applications.

4. Conclusions

In this study, CuO/n-Si heterojunction solar cells were produced by thermal evaporation. It was determined that the heterojunction structure exhibits a good rectifying properties in dark and photovoltaic properties under illumination. The best value which we achieved for conversion efficiency was 1%. This value is comparable to those of the CuO/n-Si produced by various methods in the literature [1–5]. The smallest value of ideality factor (1.82) we have obtained, indicates that the contacts of the CuO/n-Si heterojunctions are not ideal. The obtained value of rectification factor of about 17882 shows that CuO/n-Si contacts produced by thermal evaporation have good rectifying properties.

Thus, we have shown that using of thermal evaporation method in the production of CuO/n-Si heterojunction solar cells gives positive results. Thus, the thermal evaporation technique can be considered as an alternative method in the production of CuO/n-Si heterojunction solar cells.

Table 2. Some photovoltaic parameters of the CuO/n-Si heterojunction solar cells produced by thermal evaporation.

Sample name	V _{oc} [V]	I _{sc} [A]	P _{max} [W]	FF [%]	η [%]
D1	0.34	0.007658	0.00078	30	0.78
D2	0.35	0.009860	0.0010	29	1.00
D3	0.29	0.002239	0.00022	34	0.22
D4	0.34	0.003607	0.00038	31	0.38
D5	0.37	0.003472	0.00045	35	0.45
D6	0.25	0.007966	0.00044	22	0.44
D7	0.27	0.007838	0.00055	26	0.55
D8	0.27	0.010612	0.00060	21	0.60
D9	0.27	0.012121	0.00092	28	0.92
D10	0.27	0.014450	0.00074	19	0.74
D11	0.28	0.016467	0.00097	21	0.97

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