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Implications of electron beam irradiation on Al/n-Si Schottky junction properties

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ABSTRACT

The 7.5 MeV electron beam irradiation (EBI) effects on the Al/n-Si Schottky junction properties is studied in detail by analyzing I-V characteristics, power law characteristics, photoelectron spectra and energy band diagrams. The modifications in the junction parameters such as Schottky barrier height (Φ_B), ideality factor (n), and series resistance (R_S) at different irradiation doses are caused due to the formation of Al_2O_3-SiO_2 dielectric medium in the interface of Al and n-Si. As a result, Φ_B and band bending properties of the junction were modified. A linear correlation of Φ_B with EBI dose, interface trap states (m) and effective work functions (EWFs) suggests that the EBI technique is particularly advantageous for the miniature of devices which use band lineup as a key parameter in the device processing.

1. Introduction

The rectifying metal-semiconductor (MS) or Schottky junctions find number of applications in semiconductor device technology [1]. The precise relationship between the structure, chemical composition and the electrical properties at the Schottky junction is both of fundamental and technological interest. Beside interest on the bulk electronic properties, current advances in the capability of measuring precise surface and interface properties, allowed many experimental and theoretical studies on the Schottky junction [2,3]. However, the nature of Schottky interface or simply the Schottky barrier height (Φ_B) is still questionable. The detailed mechanisms involved in the interfacial region were proven to be difficult to identify due to irregularities in the arrangement of atoms lying in the interface region.

Obtaining the desirable MS junction properties or optimal Schottky barriers is crucial to the device optimization in the field of optoelectronics, microelectronics and energy conversion [1]. It is quite challenge to optimize both electronic and chemical properties for the simple metal contact to the semiconductor. Besides elemental composition, energy processing is a key macroscopic tool for achieving desirable interface properties. Such processes include furnace annealing, rapid thermal annealing with flash lamps, pulsed lasers, and electron beams [1]. The application of electron beam irradiation on the Schottky junctions could easily bring some interesting modifications in the junction properties. Since EBI affects the surface, interface and to some extent bulk electronic properties by inducing defect states [2]. Therefore, different electronic and chemical mechanisms can give rise to new junction properties that could dominate the barrier formation between metal and semiconductor.

In this paper, we report on the effect of EBI on the Al/n-Si Schottky junction properties. An in-depth analysis of current-voltage (I-V) characteristics and photoelectron spectroscopy studies is presented. The studies suggest that the modified interface chemistry could bring some interesting changes in the electrical properties of the junction. For example, the metal oxide semiconductor field-effect transistors (MOSFETs) and dynamic random access memories (DRAMs), where the band lineup at metal-insulator-semiconductor interfaces is an important design parameter [3].

2. Experimental method

The phosphorus doped Si (100) wafer having $N_D = 1.5 \times 10^{14}$ cm^{-3} was procured from Sigma Aldrich®, India. The diced ($10 \times 10 \times 0.5$ mm^3) and standard RCA cleaned n-Si wafers are deposited with Al contacts using thermal evaporation technique. The Al thickness and effective device area are kept at ~15 nm and 3.14×10^{-4} cm^{-2} respectively. The prepared Al/n-Si Schottky contacts are subjected to 7.5 MeV electron beam irradiation (EBI) using

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10 MeV linear accelerator (LINAC) present at Raja Ramanna Centre for Advanced Technology (RRCAT) India. The EBI parameters such as electron beam energy (7.5 MeV) and dose rate (6.5 kGy/s) were fixed throughout irradiation experiment. The EBI on prepared Al/n-Si Schottky contacts is performed at room temperature and at different irradiation doses (500, 1000, 1500 kGy). The other details of EBI parameters are detailed in our previous studies [2]. The I-V characterization was carried out using Keithly 2450 source meter under dark conditions. The copper pressure contacts were used as back ohmic contacts during measurements [2]. The x-ray photoelectron spectroscopy (XPS) investigations of both Si and Al/n-Si Schottky contacts were performed before and after EBI using Omicron energy analyzer (EA-125) with Al-kα (1486.7 eV) as a source of x-rays. The effective work function (EWF) measurements of Si and Al surface were carried out at 40 eV photon energy using synchrotron radiations (Indus-1 AIPES Beamline-2, RRCAT India).

3. Results and discussion

3.1. Analysis of I-V characteristics

Fig. 1 shows the I-V characteristics of Al/n-Si Schottky contacts at different irradiation doses. The variations in these characteristics at different EBI doses indicates the modified Schottky junction parameters such as Schottky barrier height (Φ_B) and ideality factor (n). These parameters are determined by applying thermionic-emission (TE) model. According to this model, the relationship between forward current (I) and applied voltage (V) [4,5].

$$I = I_s\left[\exp\left(\frac{qV}{nkT}\right) - 1\right] \tag{1}$$

$$\text{where, } I_s = AA^{**}T^2\exp\left(-\frac{q\Phi_B}{kT}\right) \tag{2}$$

is the reverse saturation current, A is effective area of the diode, A^{**} is the Richardson constant (for n-Si, $A^{**} = 112\ A\cdot cm^{-2}K^{-2}$ [4]), q is charge of the electron, Φ_B is Schottky barrier height, k is Boltzmann constant and T is absolute temperature. The parameter n in Eq. (1) is known as ideality factor, which accounts for the non-ideal behavior of Schottky diode [3,4].

For $V > 3kT/q$, the term -1 in Eq. (1) can be neglected. We obtain

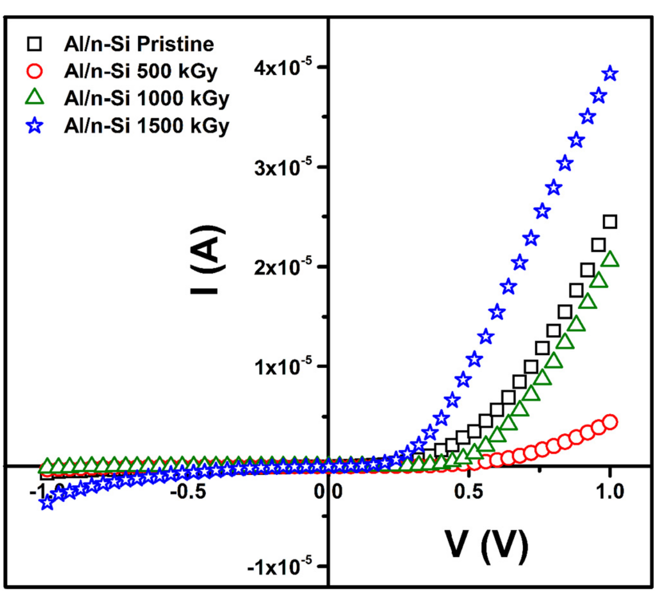

Fig. 1. I-V characteristics of Al/n-Si Schottky junctions irradiated at different doses.

Table 1
Schottky diode parameters of Al/n-Si Schottky contacts at different electron beam irradiation doses of 7.5 MeV electrons.

Diode	TE model		Cheung model		
	Φ_B (eV)	n	Φ_B (eV)	n	R_s (kΩ)
Al/n-Si Pristine	0.78	3.49	0.77	3.19	23.11
Al/n-Si 500 kGy	0.82	4.45	0.80	4.36	49.86
Al/n-Si 1000 kGy	0.84	3.20	0.86	2.65	11.85
Al/n-Si 1500 kGy	0.79	2.29	0.79	2.14	12.99

a straight line equation of the form

$$\ln I = \frac{qV}{nkT} + \ln I_S \tag{3}$$

The slope and intercept of the lnI vs. V plot gives the parameters n and Φ_B respectively. For all the Al/n-Si contacts, these parameters are extracted in the voltage range where the best line of fit (r = 0.99) was obtained in the forward lower bias voltage region.

Table 1 gives Φ_B and n values before and after EBI. The obtained values agree well with the values of the other four identically prepared and irradiated Schottky contacts. As noticed, the variations in these parameters indicates that the Al/n-Si Schottky junction is strongly affected due to the generation of EBI induced defect states and interface trap states. However, to account for the actual variation of n and Φ_B with EBI dose the effect of series resistance R_S on these parameters must be considered in the evaluation method. This can be done by applying Cheung model. According to this model, the TE model Eq. (1) for $V > 3kT/q$ takes the form [5].

$$I = I_s\left[\exp\left(\frac{q(V - IR_s)}{nkT}\right)\right] \tag{4}$$

Differentiation of Eq. (4) with respect to I gives,

$$\frac{dV}{d(\ln I)} = R_sI + \frac{nkT}{q} \tag{5}$$

The slope and intercept of the $\frac{dV}{d(\ln I)}$ vs I plot gives R_s and n respectively. On the other hand, Φ_B and R_s can be determined by plotting following relation:

$$H(I) = R_sI + n\Phi_B \tag{6}$$

where,

$$H(I) = V - \frac{nkT}{q}\ln\left(\frac{I}{AA^{**}T^2}\right) \tag{7}$$

In determining H (I) and Φ_B from above equations, it is required to consider the n value obtained from Eq. (5) plot. Also, for the better accuracy, the downward curvature region of the linear I-V characteristics (Fig. 1) must be selected [2,6].

As noticed from Table 1, the variations in Φ_B and n values between TE and Cheung model is attributed to the effect of R_s which was not considered in the TE model. Primarily, R_s is originated from the presence of a thin oxide layer between Al and n-Si interface as well as contribution from the bulk n-Si. Due to high value of R_s and $n > 1$, the Al/n-Si contacts are exhibiting non-ideal I-V characteristics. However, variation in their values after EBI is a consequence of modified nature of interface properties between Al and n-Si.

3.2. Power law characteristics

It is well-known that, the ideality factor (n) is simply the manifestation of the homogeneity of interface. For an ideal homogeneous interface n must be unity. However, most practical Schottky contacts exhibit greater than unity ideality factors. This is due to inhomogeneous nature of the interface or barrier Φ_B [7]. In the present case, $n > 1$

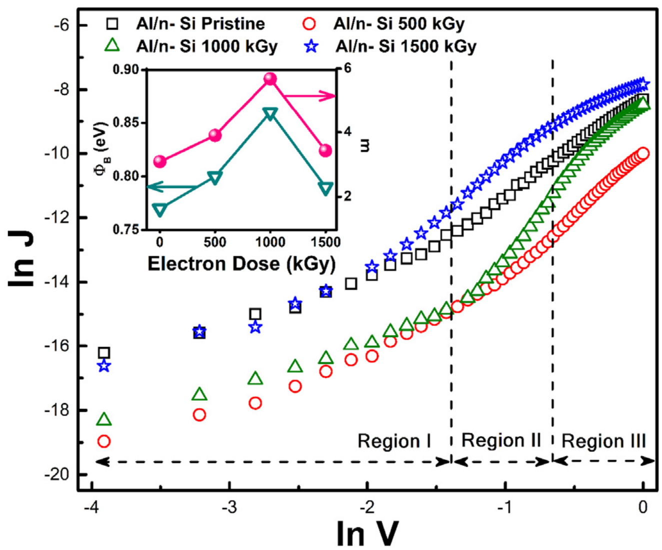

Fig. 2. Power law characteristics of Al/n-Si Schottky junctions irradiated at different doses. The inset plot shows power of the voltage (m) and Φ_B variation at different irradiation doses (m variation is determined from the slope of the Region II).

indicates the Φ_B inhomogeneity across Al/n-Si junction. This will lead to the participation of different transport mechanisms across the biased Al/n-Si junction. As a result the obtained I-V characteristics does not follow the TE model Eq. (1). Therefore, when the junction interface is inhomogeneous it is quite difficult to conclude on the TE of electrons or the other transport mechanisms that are taking place for a certain range of voltage. Instead, it is possible to realize the dominant type of transport mechanism for a certain range of voltage range by plotting the power law characteristics [8,9]. According to power law, the current density across the junction varies as power m of the applied voltage V i.e., $J \propto V^m$ where J is the current density and m is a slope parameter. Therefore, the plot of lnJ vs. ln V gives a straight line having a slope value of m. Fig. 2 shows the lnJ vs. ln V plots before and after EBI at different irradiation doses. The three clear and distinct voltage regions (Region I, Region II and Region III) are noticed for all the irradiation doses. The voltage range of the each region is approximately separated by the dotted lines. The slope value m in the each region gives information on the dominant type of transport mechanism [8].

In the Region I (or lower voltage region), the slope m values are found to vary in the range 1.3–1.7 for all EBI doses, suggesting that thermionic emission (TE) of electrons over the barrier Φ_B is a dominant type of transport mechanism. However, in the Region II (moderate voltage region) it is noticed that, the current density (J) is found to vary with a certain power m value of the voltage V for each EBI dose. For the un-irradiated Al/n-Si Schottky contact m = 2.8 but for the irradiated contacts, the m value is greater than this value. The variation is shown in the inset of Fig. 2. Therefore in the Region II, the power m > 2 indicates an exponential distribution of interface trap states. As a result of which the space charge limited conduction (SCLC) process is expected to takes place and it is dominating over the TE of electrons over the barrier in the Region II [8,9]. This is also true for the Region III, where m varies in the range 1.7 to 3.3. But the decrease in range of m values suggests the transition from trap filled SCLC to free carrier SCLC. If this must be happening, then the voltage range of Region III (0.7 to 1.0 V) of lnJ − ln V plot and the same voltage range (0.7 to 1.0 V) in the I-V plot (Fig. 1) should display linear variation of V and I. This suggests that the variation of V and I follows Ohm's law with constant (R_s). In addition to these transport processes, a small contribution from the tunneling and tunneling through the trap states mechanisms cannot not be ignored [3]. Overall, these different conduction mechanisms due to barrier inhomogeneity explains the deviation from TE model Eq. (1).

In addition to above, a strong correlation was found between m and Φ_B at different EBI doses as shown in the inset of Fig. 2. It is observed

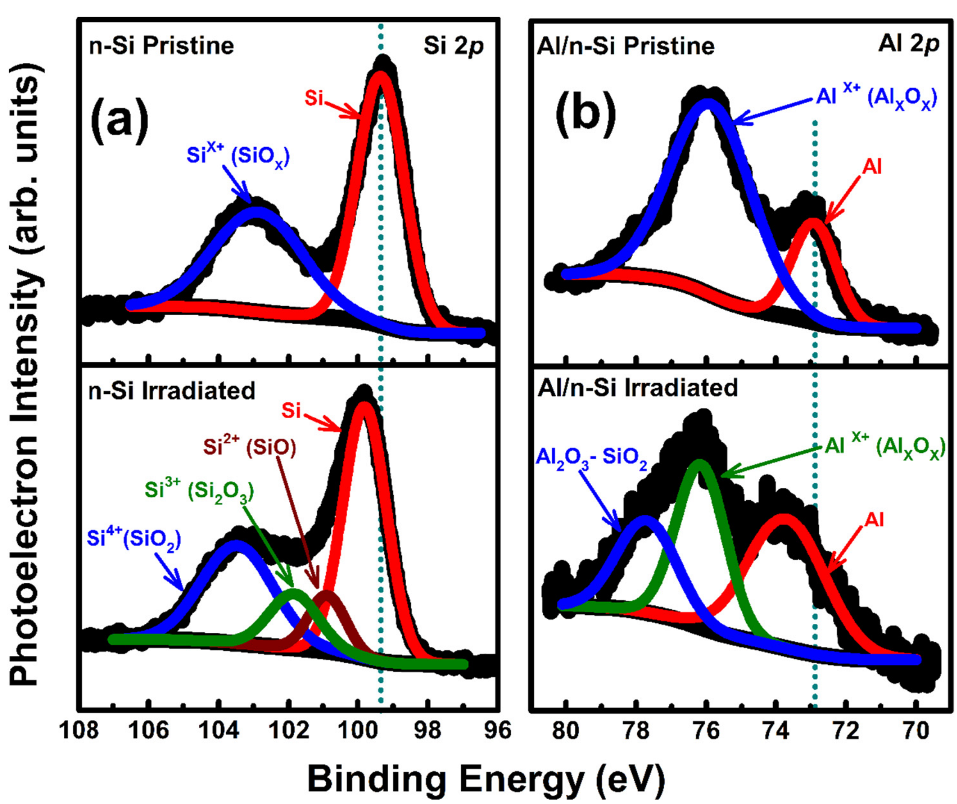

Fig. 3. (a) Si 2*p* core XPS spectra of pristine and irradiated n-Si wafer (b) Al 2*p* core XPS spectra of Al/n-Si Pristine and irradiated Al/n-Si Schottky contact at 1500 kGy.

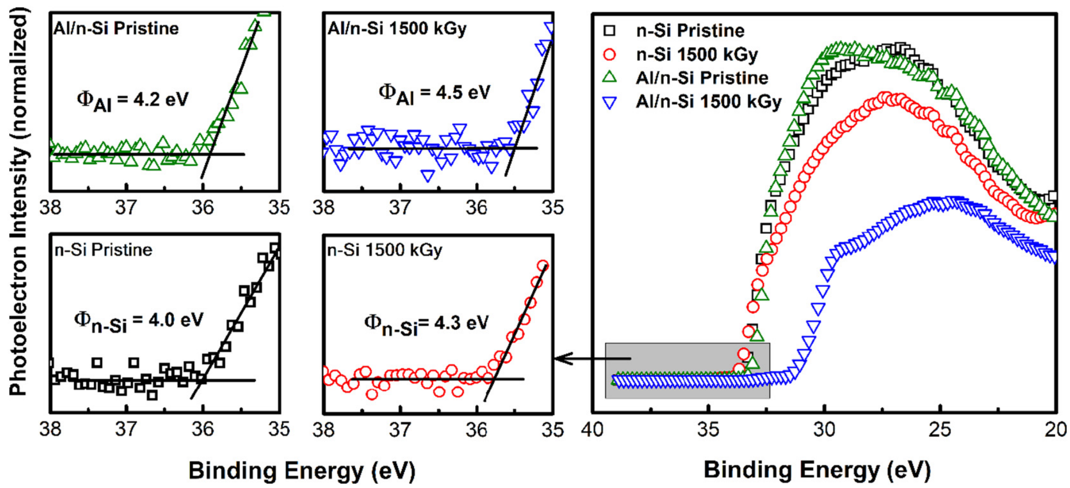

Fig. 4. Photoelectron spectra of Si and Al on n-Si (Right side) before and after electron beam irradiation. The effective work functions (EWFs) are determined from the secondary energy cut-off region (left side) of the spectra.

that both m and Φ_B are displaying similar variation at different irradiation doses. This infers that Φ_B strongly depends on the irradiation induced trap states. The slope parameter m represents the interface trap states, greater the value of m, the greater is the exponential distribution of interface trap states between Al and n-Si. This will result in greater value of Φ_B due to the shift in the Fermi level (E_F). The interface trap states in the present case include the dangling Si—O [10] and Al—O bonds. These trap states act either as acceptor or donor depending on their position with respect to E_F. However, the increase in Φ_B with m suggests that the most of the interface trap states are essentially of acceptor in nature i.e., below the E_F, as a result there will be an increase in the effective Schottky barrier height (Φ_B).

3.3. XPS analysis

In addition to the analysis of I-V characteristics, the XPS investigations is also carried out separately for the irradiated n-Si wafers and Al/n-Si Schottky contacts. Fig. 3 (a) shows the Si 2*p* core XPS spectra of the un-irradiated (pristine) and irradiated n-Si. The Si 2*p* binding energies for the pristine and irradiated n-Si wafers are observed at 99.3 eV and 99.8 eV respectively. The broad shoulder on the higher binding energy side of the n-Si Pristine is resulted from Si bonding with ambient oxide (SiO_x). But the observed Si 2*p* chemical shift of 0.5 eV and the shoulder increase in the irradiated n-Si is caused due to the generation of various oxidation states of Si such as Si^{2+}, Si^{3+} and Si^{4+}. The Gaussian decomposition of the spectra showed the irradiation induced Si^{2+}, Si^{3+} and Si^{4+} states at 100.9, 101.8 and 103.5 eV respectively. Similar intermediate oxidation states after electron irradiation on MOS structure of SiO_2 was reported by Grunthaner et al. [11] and it is also supported by empirical tight binding approximation [12,13].

The above EBI induced intermediate oxidation states of Si plays crucial role in altering the Al/Si junction properties. This can be clearly seen from Fig. 3 (b), where the Al 2*p* core XPS spectra of the un-irradiated (Al/n-Si Pristine) and irradiated Al/n-Si contact is shown. As noticed, the distortions after EBI including the significant metallic Al 2*p* binding energy shift from 72.9 to 73.7 eV and width variations strongly suggesting the modified nature of Al/n-Si junction. The high-energy electrons penetrate the Al/n-Si junction completely and causes the ionization damage in the interface as well as bulk. The thin interfacial oxide layer between Al and Si gives rise to different oxidation states as described above and moves outward due to thermal agitation, and on the other hand the Al atoms will penetrate into the interface. In this process of Al inter diffusion and outward diffusion of SiO_x, causing the bonding between Al and SiO_x states when the irradiation lasted. This bonding between Al and SiO_x chemical species leads to the interfacial oxidation between Al and n-Si. The Al atoms in the interface oxidizes and forms Al_2O_3 due to their interaction with Si^{2+} and Si^{3+} states, while the Si^{4+} states (SiO_2) remain unaffected. This is in accordance with the in-situ PES studies of Al/SiO_2 structures, where the authors report that formation of Al_2O_3 in the interface is governed only by the sub oxides of Si other than SiO_2 [14]. These observations suggest that the Al_2O_3 and SiO_2 in the interface together form a dielectric Al_2O_3-SiO_2 medium in the interface of Al/n-Si junction. This causes the significant Al 2*p* metallic chemical shift after irradiation. The Gaussian decomposition of Al 2*p* spectra showed the Al_2O_3-SiO_2 chemical state at binding energy of 77.7 eV as shown in Fig. 3 (b). Therefore these Al—O and Si—O bonds in the interface acts as interface trap centers, which influence the band bending properties and Schottky barrier height, Φ_B (Section 3.2).

3.4. Effective work function measurements

In addition to the XPS analysis of the Al/n-Si junction interface, the effective work function (EWF) measurements on the sample surface are also carried out using photoelectron spectroscopy (PES) technique. Fig. 4 shows the photoelectron spectra of Si wafer and Al/n-Si junction which is carried out separately before and after irradiation. The spectra is taken at 40.0 eV photon energy using Synchrotron radiation. The outline of the procedure to determine effective work function (EWF) is shown on the left side of the Fig. 4. The point of intersection as shown by the horizontal and slanted vertical line is equal to binding energy at the secondary energy cut-off (E_{BO}). Below this critical point of E_{BO}, the kinetic energy of the photoelectrons are essentially zero, and above this one measure the spectral scale corresponds to the point at which excitation from states at the sample vacuum level would occur. In other words, secondary edge cut-off point (E_{B0}) represents the electrons that had just enough energy on arrival at the surface to overcome EWF. Hence one can determine EWF simply by subtracting E_{B0} from the given excitation photon energy. The EWF of n-Si is given by $\Phi_{n-Si} = (40.0 - 36.0)$ eV. Here 40.0 eV is the excitation photon energy and 36.0 is the E_{BO} of secondary energy cut-off point. In the similar way, the EWF of Al and n-Si were determined before and after EBI [15,16]. The EWFs of pristine and irradiated n-Si wafer (without Al contact) is 4.0 and 4.3 eV, and the EWF of Al on pristine and irradiated Al/n-Si surface is 4.2 and 4.5 eV respectively. The modification in EWFs of Al and n-Si is a consequence of EBI induced effects such as modified surface (and interface) chemistry. Although the EWF of Al and n-Si were determined separately, the EWF of the Al/n-Si interface could be entirely different due to different interfacial chemistry. Further it cannot be determined

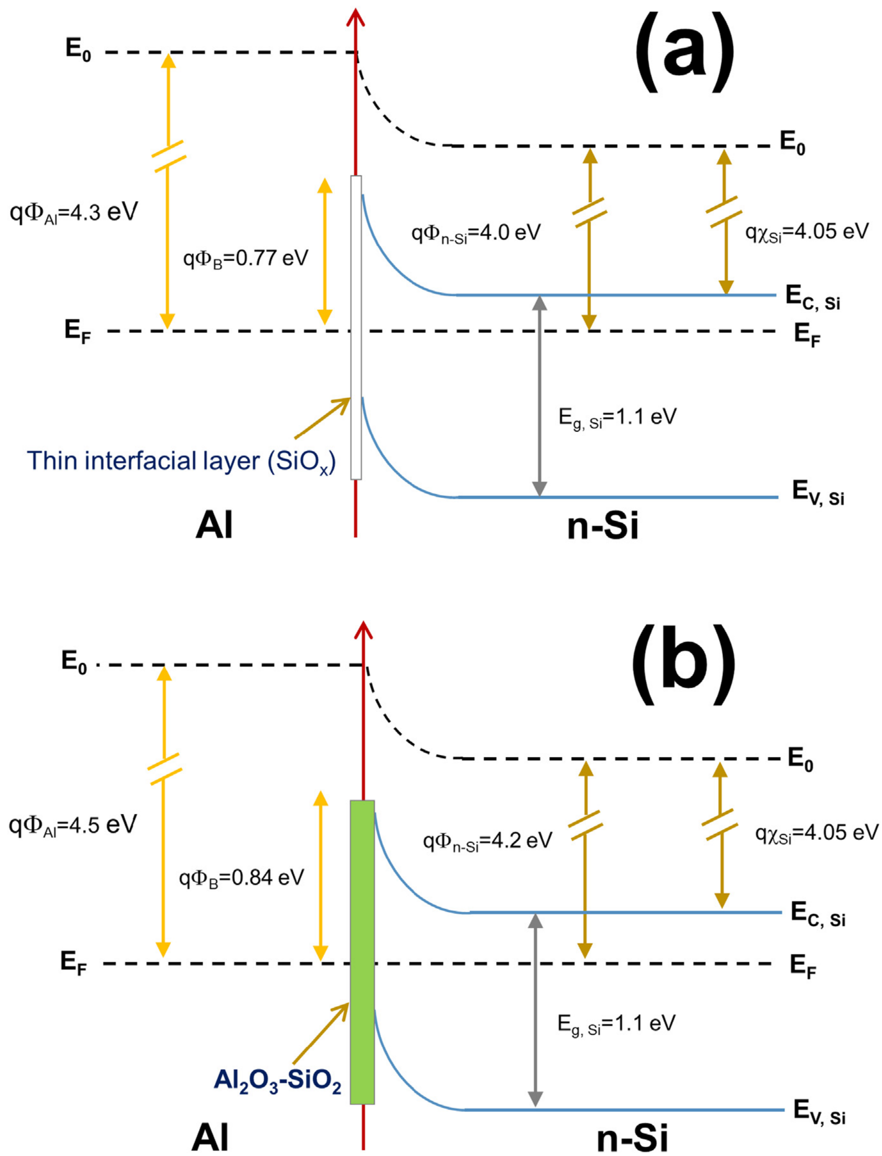

Fig. 5. Schematic representation of energy band diagram of Al/n-Si Schottky junction at equilibrium condition (a) before irradiation (b) after irradiation- showing the formation of irradiation induced Al_2O_3-SiO_2 dielectric interface. E_0 is the vacuum level, E_F the Fermi level, $q\Phi_{Al}$ and $q\Phi_{n-Si}$ are the effective work functions of Al and n-Si respectively, $E_{V,\ Si}$ is the valence band edge of n-Si, $E_{C,\ Si}$ is the conduction band edge n-Si, $E_{g,\ Si}$ energy band gap of n-Si, $q\Phi_B$ is the Schottky barrier height, $q\chi_{Si}$ is the electron affinity of Si.

accurately at the interface due to the low escape depth of photoelectrons. However, modified EWF of Al and n-Si before and after EBI would certainly influence the band lineup at their interface and consequently the junction properties.

3.5. Energy band diagram of Al/n-Si Schottky junction before and after EBI

The schematic representation of energy band diagrams of un-irradiated Al/n-Si and irradiated Al/n-Si Schottky junctions at equilibrium are shown in Fig. 5 (a) and (b) respectively. The explanation of the energy band diagram is adapted from the Ref. 4. The energy level which is common to Al and n-Si is known as vacuum level (E_0), at this level the energy of electron is assumed to be free from the influence of Al and n-Si. The energy difference between E_0 and E_F is known as work function ($q\Phi$). As determined from the photo electron spectra (Fig. 4), the EWF of Al is greater than that of n-Si ($\Phi_{Al} > \Phi_{n-Si}$) i.e., $E_F$of n-Si is lies near to the E_0 compared to E_F of Al. In Al or for any given metal, E_F is located above its conduction band and at a fixed separation from E_0. But in n-Si, E_F is not fixed as it depends on the doping concentration. When Al comes in contact with n-Si, due to concentration gradient there will be the movement of electrons from n-Si to Al and Al to n-Si until the net current density is zero i.e., when equilibrium is reached and the E_F have aligned. As a result, n-Si is charged positively with respect to Al and deforms the band structure. The band bending of $E_{C,\ Si}$ is accompanied by an identical bending of the E_0 in n-Si such that the locus constant E_0 has not changed. The potential barrier which is set up on the n-Si side prevents further the motion of electrons from n-Si to Al, while the barrier which is set up on the Al-side is called the Schottky barrier height ($q\Phi_B$), which prevents the motion of electrons from Al to n-Si. When the junction is biased, barrier on n-Si side will vary but $q\Phi_B$ remain unaffected. Therefore $q\Phi_B$ basically controls the junction properties.

A thin interfacial layer is always present between metal and semiconductor. The interfacial layer as shown for the un-irradiated case (Fig. 5 (a)) is usually assumed as transparent to electrons for thickness in the range of few angstroms [3]. In the present case, the ideal Schottky-Mott rule: $q\Phi_B = q(\Phi_{Al} - \Phi\chi_{Si})$ is not satisfied due to the presence of thin interfacial layer or interface trap states or due to the presence of defect states [3,4,7]. However, the nature of interface before and after EBI is completely different. This is already described from XPS analysis (Section 3.3). For the un-irradiated Al/n-Si junction, the interface states are intrinsic and they would be generated prior to Al deposition on n-Si. But for irradiated Al/n-Si, the chemical interactions exist on an atomic scale produces new chemical structure Al_2O_3-SiO_2. The resulting dipole layer will therefore modify the band bending properties across Al/n-Si junction. Fig. 5 (b) shows the schematic representation of the influence of Al_2O_3-SiO_2 dielectric medium on the band-bending properties of the Al/n-Si junction. The Al_2O_3-SiO_2 is a high-κ dielectric interface that has good chemical and thermal stabilities. It also offers high barrier offset for the electrons and holes [17]. The strength of interfacial bonding determines the type of electrically active sites altering the band bending. Therefore, the precise energy position of E_F within the band gap and the $q\Phi_B$ value depends on the distribution of interface states. As a result the degree of band bending and $q\Phi_B$ will depend on irradiation dose and the variations in the interface trap states, m (inset, Fig. 2).

4. Conclusion

The 7.5 MeV electron beam irradiation (EBI) effects on Al/n-Si Schottky junction properties is studied at different EBI doses. A detailed analysis of the current-voltage (I-V) characteristics and photoelectron spectra showed that the junction properties are greatly modified due to the formation of Al_2O_3-SiO_2 dielectric medium at the junction interface. The Φ_B of the Al/n-Si junction is found to depend on the EBI dose, interface trap states and effective work functions. Thus the modification in the interface chemistry by EBI technique suggests that it could bring significant differences in the electrical properties of the devices which use Al/n-Si Schottky structures.

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