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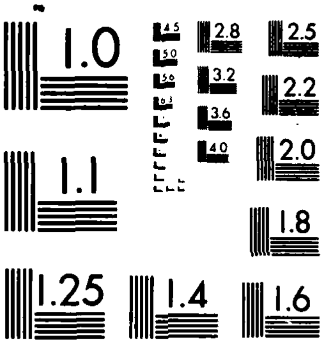

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COMPARATIVE STUDIES OF ELECTRON AFFINITIES AND WORK FUNCTIONS FOR GaAs AND Si

by

Xing Yirong

EDITED TRANSLATION

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Comparative Studies of Electron Affinities and Work Functions for GaAs and Si

Xing Yirong
Institute of Semiconductors, Chinese
Academy of Sciences

W. Ranke
Fritz-Haber-Institute of Max-Plank-Society

Abstract

Ultra-violet Photoemission Spectra (UPS) involving core level photoemission peaks (Ga 3d for GaAs and Si 2p for Si) is measured for the (111), (110), $(11\bar{1})$, and $(00\bar{1})$ surfaces of GaAs and Si using the light from a Helium lamp (21.2 eV and 40.8 eV) and from the Berlin synchrotron radiation source BESSY (108.6 eV), respectively. These surfaces are prepared by ion bombardment and annealing on cylindrically shaped GaAs and Si crystals with $[\bar{1}10]$ as their axis. The GaAs cylinder is in addition prepared by molecular beam epitaxy yielding As-rich phases on $(11\bar{1})$ and $(00\bar{1})$. The work function $\overset{\text{Phi}}{\phi}$ and the electron affinity χ are evaluated from the low energy (secondary electron) threshold and the energy position of the core level photoemission peak. It is shown that due to the crystal polarity and differences in surface composition, the electron affinity depends strongly on

the orientation for CaAs. For Si, the missing bulk polarity is responsible for the small variations of χ, which may be caused by the different surface reconstructions. On GaAs, the Variation of $\overset{\text{Ph.}}{\phi}$ and χ are essentially parallel indicating no strong band bending variations. On Si, however, the relatively strong variations of $\overset{\text{Ph.}}{\phi}$ indicate strong variations of the band bending.

I. Introduction

The change of work function ϕ of metals reflects the electric dipole of atoms in the surface layer. Both theory and experiment have proved [1,2] that the value ϕ is related to the crystalline orientation; it has the maximum value in the closed-packed plane and decreases with the decreasing of atomic density. For example, the ϕs of tungsten in different crystal planes can have a difference of about 20%[2]. This phenomenon can be explained by the smoothing effect of distribution of surface charge density[1]. Specifically, the distribution of positive ions in the Wigner-Seitz primary cell is uniform. In order to minimize the total energy, the moveable electronic charges will relax and produce the surface electric dipole which decreases the work function and is crystalline orientation dependent.

For semiconductor crystallines, it is the change of the electron affinity χ of electrons that reflects the surface electric dipole. GaAs is partially-polarized compound . The change of χ is mainly attributed to the crystalline polarity and surface composition, and the smoothing effect of surface charges is not important[3]. But for unpolarized covalent semiconductor Si, how will χ change with the crystalline orientation? Does the smoothing effect of surface charges affect it? This paper will answer these questions, and the pinned positions of Fermi energy of several low-index surfaces of GaAs and Si will be given.

2. Principles of Measurement

The electronic affinity, work function, surface Fermi energy and other parameters are determined by photoemission spectroscopy. The principle of this technique is shown in Fig. 1.

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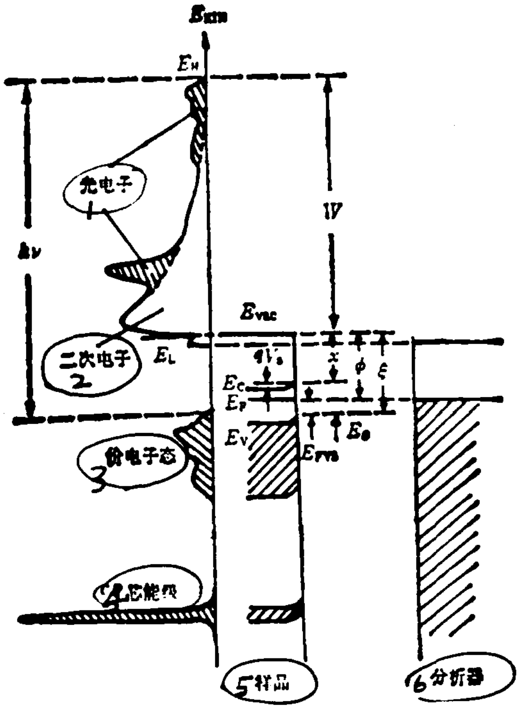

Fig. 1. The principle of determining electronic affinity, work function, and other parameters with photoemission spectroscopy.

$h\nu$ - Energy of incident photons, E_{kin} - Kinetic energy of photo electrons, W - the total width of the photo electron spectrum, E_L - Threshold of second electrons, E_H - High energy threshold, E_{vac} - Vacuum energy level, E_C - Energy of bottom of conduction band, E_V - energy of top of valence band, E_g - Width of forbidden zone, E_F - Fermi energy, E_{FVS} - Surface Fermi energy, χ - Electronic affinity, ϕ - work function, ξ - Ionization energy, qV_S - Surface potential barrier.

1 - Photoelectron; 2 - Second electron; 3 - States of valence electrons; 4 - Core states; 5 - Sample; 6 - Analyzer.

The change of high energy (electron kinetic energy) threshold E_H directly gives out the change of surface potential barrier qV_s, that is:

$$\Delta E_H = \Delta(qV_s) \qquad (1)$$

The threshold of low energy (second electron) of photo electrons, E_L, directly reflects the change of work function O, that is:

$$\Delta E_L = \Delta\emptyset = \chi + \Delta(qV_s) \qquad (2)$$

If E_L and E_H are measured simultaneously, we can obtain the relative change of electron affinity $\Delta\chi$, that is: $\Delta\chi = \Delta E_L - \Delta E_H = \Delta(E_L - E_H)$ (3)

From Fig. 1. we also can learn that if the energy of the incident photons is known, χ (or the ionization energy) and O can be calculated using the total width W of photoemission spectrum and qV_s. That is: $\chi = h_V - W - E_g$ (or $\xi = h_V - W$) and $\emptyset = \xi - (E_F - E_V)_b + qV_s$. where $(E_F - E_V)_b$ is the difference of the bulk Fermi energy E_F and the energy of the top of valence band. As soon as the values of ξ and $\emptyset$ are known, the pinned position of surface Fermi energy can be obtained. That is the difference of E_F and E_V in the surface: $E_{FVS} = (E_F - E_V) = \xi - \emptyset$. The value of qV_S can be determined according to the known value of $\emptyset$.

In the experiments, it is difficult to measure the position of the top of the valence band precisely. The reason is the overlapping of the photoemission of the valence band and the photo electrons from the intrinsic surface states and defect states which are dependent on the crystalline orientation. In order to overcome this difficulty, we can measure the energy of some gap states, E_i, (E_i and E_V are known and are constant) as the reference energy, instead of the measurement of the high energy threshold (the position of E_V). For GaAs, E_i is usually chosen as the 3d of Ga[4]; for Si, no such kind of measurement has been reported, and 364 we chose 2p. The difference of Ga 3d and the top of the valence band is 18.81+0.02 eV[4]. We used He II (40.8 eV) and He I (21.2 eV) as light sources to measure the peak values of Ga 3d photo electrons and the second electrons of GaAs, respectively. The energy level of $2p_{3/2}$ of Si is 98.74 eV[5] below the top of the valence band; the correspondent photoemission spectrum was measured with the synchrotron radiation at BESSY (Berlin) as light source (h_V=108.6 eV was selected by a SX-700 monochromater). The photo electrons measured in this method are mainly from the first several atom layers under the surface and its thickness is far less than Debye length. The depth of measurement for Si is a little larger in order to decrease the contribution of the most outside layer of the atoms because experiments have already shown[6,7] that 2p energy level of Si at the most outside layer has chemical displacement.

3. Experiment

GaAs samples are Te-doped n-type single crystals ($n \sim 6 \times 10^{17}$ cm^{-3}), and Si samples are B-doped p-type single crystals ($p \sim 2 \times 10^{17}$ cm^{-3}). In order to obtain different crystalline orientations, both type samples are cylindrically shaped with diameter of 23 mm, height of 10 mm, and with $[\bar{1}10]$ as axis. The structure of sample holders can be referred to [8]. The surface of Si was cleaned by bombardment of Ar ions (1keV) plus annealing (1050 - 1100 K), that is IBA surface. The surface of GaAs was cleaned with two methods: (a). IBA surface obtained by the bombardment of Ar ions plus annealing (~800 K), (2). molecular beam epitaxy method[9] with single evaporation furnace (loaded with GaAs) to prepare MBE surfaces on above IBA surface.

The experimental arrangement is a multifunction electron spectrometer including a LEED system, a AES, and a UPS system with binocular cylinder analyzer, and an ion gun for sputtering disposal. All the measurements were carried out in 10^{-9} - 10^{-10} Torr ultra-high vacuum. The results of AES and LEED measurements show that both GaAs and Si have a clean and ordered surface. For the IBA surface of GaAs, (111) surface is (2X2) reconstructed; this agrees with [10]. (110) surface is (1X1) structure. The diffraction spots of

$(11\bar{1})$ and $(00\bar{1})$ surfaces are comparatively weak and the background is brighter; these indicate that the concentration of defects is comparatively high. For the MBE surfaces of GaAs, the atomic structure of (111) and (110) is the same as IBA surfaces, and $(11\bar{1})$ and $(00\bar{1})$ clearly show As-rich (2x2) and C (2x8) reconstructed, respectively. This agrees with the result of literature [11] and [12]. For the IBA surfaces of Si, the LEED patterns of (111) and $(11\bar{1})$ surfaces (they are same) have the typical (7X7) reconstruction structure, and $(00\bar{1})$ is (2X1) reconstructed. These results agree with most experimental results of other people. But for (110) surface, although the integer and non-integer spots can be observed, we could not distinguish whether it is a (4X5) room temperature phase or a (2X1) high temperature phase[13]. The small planes which are neighbors of (110) also possibly exist.

4. Results and Discussion

Fig. 2 and Fig. 3 are the photoemission spectra of MBE surfaces of GaAs and the IBA surface of Si, respectively. It can be seen that the low-energy sides are all relatively steep, and this indicates that it is easy to determine the low-energy threshold, which reflects the change of work function. Because the photo electron peaks of 3d of GaAs and

2p of Si are asymmetric, in order to measure the changes of their positions the most precise reference point is not the maximum of the peak but the position of the half height on the high energy side. The relative error of this measurement is the same as the case of determining the low-energy threshold: For GaAs, it is estimated as =0.03 ev and for Si it is estimated as ±0.015 eV.

The χ, ϕ and E_{FVS} of several low-index crystalline surfaces of GaAs and Si, determined with the above method, are listed in table 1. The values of ξ are not listed, but it can be determined easily by use of the sum of X and E_g, the value of E_g at room temperature is used: E_g(GaAs)=1.42 eV and E_g(Si)=1.12 eV [14]. The positions of the core levels relative to the top of the valence band are not fully the same in the literature; for example, the maximun deviation of the Si-2p is several tenths of 1eV. Furthermore it is difficult to obtain a precise value of the incident light from SX-700 monochromator. When we determine the absolute values in table 1., with reference to literature the following values were calibrated: for Si - (001)-(2X1) surface, ϕ = 4.87 eV and E_{FVS} = 0.46 eV[15], therefore ξ = 5.33 eV; for GaAs-(110)-IBA surface, E_{FVS} = 0.75 eV[16]. The later correction assumes that there are a great number of defect states in the (110) surface of GaAs,(prepared with IBA method). These defect states lead to Fermi energy being pinned. Such 365 assumption is not very reasonable and produces some errors for the absolute value E_{FVS}, but the relative relation with the crystalline orientation is still correct.

Different from the experimental results[2] of metals, the electronic affinities and work functions of GaAs in [111] and [11$\bar{1}$] are obviously different. For example, in MBE surfaces, $\chi_{(11\bar{1})}$ is 0.42 eV greater than $\chi_{(111)}$ and is equal to the value in the close packed (110) plane, that is $\chi_{(11\bar{1})}$ = $\chi_{(110)}$ = 4.18 eV. These results indicate that in the surfaces of GaAs, the decisive factor for the changing characteristic of χ is not the smoothing effect of the surface charges, but the polarity of crystalline[3]. (11$\bar{1}$) plane and (111) plane are terminated by As atoms (negatively charged) and Ga atoms (positively charged), and this is the cause which makes $\chi_{(11\bar{1})}$ larger than $\chi_{(111)}$. Because the surface composition of GaAs depends on the method of surface preparation, (11$\bar{1}$), (00$\bar{1}$), and (001) surfaces of MBE method are As-rich and are different from the surfaces prepared with 366
the IBA method. The $\chi_{(11\bar{1})}$ and $\chi_{(00\bar{1})}$ of MBE method are obviously larger than the correspondent values of IBA surfaces (see table 1) and this also indicates that for different crystalline surfaces, the changes of χ and ϕ are almost parallel, This indicates that the bending of the surface energy bands are basically the same.

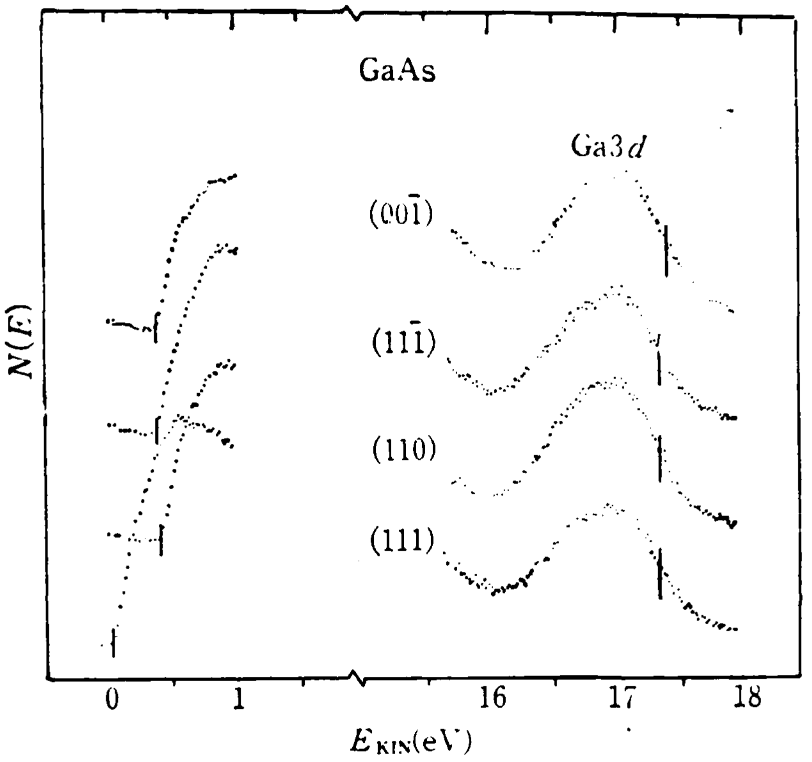

Fig. 2 The photoemission spectra of GaAs-MBE surfaces, in the vicinity of the second electron and Ga 3d, with He I and He II as light sources.

Short vertical lines are the positions of the threshold and the positions of the high energy side of Si 2p. The abscissa and ordinate are the kinetic energy of photo electrons E_{KIN} and the relative intensity N(E), respectively. The zero point of E_{KIN} is chosen as the low energy threshold of (111) surface.

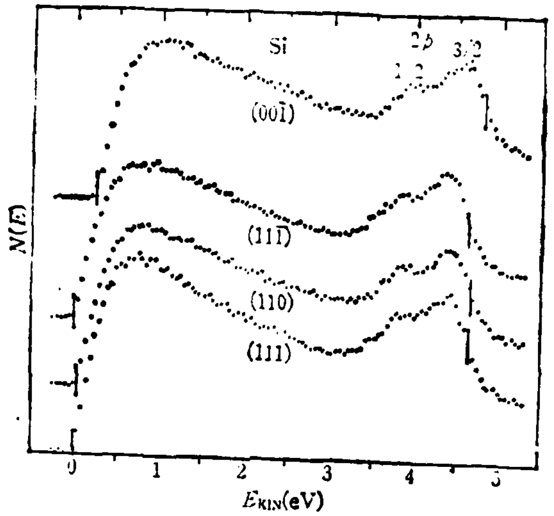

Fig. 3. The surface photoemission spectra including the threshold of second electrons, measured with monochromatic synchrotron radiation light source (108.6 eV).

Short vertical lines are the positions of the threshold and the positions of half height of the high energy side of Si-2p. The abscissa and ordinate are the kinetic energy of photo electrons E_{KIN} and the relative intensity N(E) respectively. The zero point of E_{KIN} is chosen as the low energy threshold of (111) surface.

Table 1. Values of the electron affinities χ and work functions ϕ of GaAs and Si, and surface Fermi energy E_{FVS} (unit is eV).

I 晶向	χ			ϕ			E_{FVS}		
	GaAs		Si	GaAs		Si	GaAs		Si
	IBA	MBE	IBA	IBA	MBE	IBA	IBA	MBE	IBA
111	3.69	3.76	4.14	4.35	4.45	4.59	0.76	0.73	0.67
110	4.18	4.18	4.14	4.85	4.86	4.65	0.75	0.74	0.61
11$\bar{1}$	3.91	4.18	4.14	4.58	4.91	4.59	0.75	0.69	0.57
00$\bar{1}$	3.72	4.12	4.21 4.23*	4.45	4.82	4.87	0.69	0.72	0.46

* Results of measurement on (001) surface

I - Crystalline orientation

For non-polarized crystal Si, $\chi_{(111)}$, $\chi_{(110)}$, and $\chi_{(11\bar{1})}$ are all equal to 4.14 eV, $\chi_{(00\bar{1})}$ is little larger and equal to 4.21 eV. We also determined that $\chi_{(001)}$ is equal to 4.23 eV. That is , the value of χ in Si-[001] direction is about 0.08ev higher than the values in [111] and [110] directions. This difference is small, but it is repeatable for several measurements, and it is not error an error of measurement. Different from X, the values of O have relatively obvious changes (see table [illegible]; this should be attributed to the change of the surface potential.

The experimental result that different crystalline surfaces have almost the same χ value indicates that the smoothing effect of surface charges is not important for Si. In metals, the distribution of the valence electrons in Wigner-Seitz primative cells is uniform, but in covalent crystals, the valent electrons mostly distribute in the 367 direction of bonds. This is possibly the reason the smoothing effect of the surface charges decreased obviously.

The value of χ in Si (001) is a little higher. This way be related to the surface electric dipole which is produced by the atomic reconstruction. In the recent 20 years, people suggested many models to explain the (2x1) atomic reconstruction in Si (001) surface. The calculation of total energy indicates that the symmetric dimer model is the most stable one [17]. Usually the reconstruction of atoms will cause the reimpurization of valent electrons and then cause the change of distribution of electrical charges. In the asymmetric dimer model of Si (001)-(2X1), the two paired atoms in the surface layer move towards the inside by 0.08 Å and 0.53 Å, respectively, and 0.35 - 0.45 e electrical charges have been moved to the top atoms from the bottom atoms[17]. As a result, an electric dipole is formed in the surface which increases the electronic affinity. Si (111)-(7X7) surface was also studied intensively. But because the reconstruction unit is large, it increases the complication of the problem. Therefore the result of calculation is not as mature as in the case of (100)-(2X1). The overall opinion is that there is also an electric charge transfer which accompanies the moving up and down of atoms. Chadi et al assumed that the charge transfered is about 0.[illegible] e[18], which is a little smaller than that in the case of (001)-(2X1) reconstruction. Different reconstructed surfaces have different surface electric dipole; this is possibly the cause which leads to the smaller value of χ. Furthermore, surface terraces will also produce an auxiliary electric dipole and then change the electron affinities or ionization energy[19,20]. Especially in the cases of the neighbor crystal surfaces or high index crystalline surfaces, the influence of the surface terraces will be important.

5. Conclusion

Compared with metals, the change of electron affinities of GaAs and Si is relatively small. For GaAs, the relative change between different crystalline orientations is about 10%. Considering the surface electric dipole is due to the change of surface composition (Ga and

Si), the behavior of χ can be explained. At least the smoothing effect of surface charges, which is a decisive effect for metal surfaces, is not important for GaAs. Different from GaAs, the low-index crystalline surfaces of Si have approximately similar electron affinities and only increase a small amount in (001) surfaces. This indicates that the smoothing effect of surface charges in Si surfaces is negligible. The tiny change of χ may be related to the surface atomic reconstruction or the electric dipole produced by surface terraces. As for the bending of surface energy bands, they are approximately the same in the several crystalline planes of GaAs under study, but for Si, there are relatively obvious changes.

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