Ionization-energy dependence on GaAs(001) surface superstructure measured by photoemission-yield spectroscopy

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The ionization energies for GaAs(001) are determined by photoemission-yield spectroscopy as a function of surface superstructure. The ionization energy changes by as much as 0.5 eV in accordance with the surface superstructure.

The GaAs(001) surface has received much attention because of its scientific and technological importance. GaAs(001) is a polar surface, and as such it exhibits various surface superstructures depending on surface stoichiometry. It has been confirmed that the listing of GaAs(001) superstructures in order of increasing As coverage is as follows: Ga-rich (1×1), (4×6), $c(2 \times 8)$, $c(4 \times 4)$, and As-rich (1×1).[1] Among GaAs surfaces with different surface superstructures, fairly large similarities have been found in both atomic structure[2] and surface band structure.[3] However, the work function, as determined by contact potential difference measurements, was found to strongly depend on the surface superstructure.[4] It has also been pointed out that the greatest care must be taken in the interpretation of work-function variations, since they may be due to the combined effects of, first, a change in band bending, via a change in surface-state density and position, and secondly a change in electron affinity, which strongly depends on the surface dipole.[4] Since these two kinds of changes are independent of each other, it is necessary to directly measure the ionization energy $(\phi_{h\nu})$ for these surfaces.

This paper reports the measured ionization energy for the GaAs(001) surface as a function of surface superstructure. Ionization energies are determined by photoemission-yield spectroscopy, which is a direct and accurate measurement of the photoelectric threshold.[5,6] It is found that the ionization energy varies by as much as 0.5 eV depending on the surface superstructure.

Samples used here were grown on (001)-oriented n^+-type GaAs substrates by molecular-beam epitaxy (MBE). For determining the ionization energy, first, 1-μm-thick undoped GaAs layers were grown. Then surface superstructures, including Ga-rich (1×1), (4×6), $c(2 \times 8)$, $c(4 \times 4)$, and As-rich (1×1) were fabricated on the surfaces by controlling both the surface temperature and the Ga- to As-pressure ratio at the surface after Ref. 7. Hereafter, Ga-rich (1×1) and As-rich (1×1) are referred to as Ga (1×1) and As (1×1), respectively. The produced surface superstructures were confirmed by high-energy electron diffraction *in situ*.

For the ionization-energy measurements, the samples were brought to an analysis chamber via an ultrahigh vacuum transfer chamber with base pressure of 5×10^{-10}

Torr within 2 min after fabrication to ensure that the sample surfaces would not become contaminated, which could have altered the measured ionization energy.[6] The photoelectron spectrum was measured by a sector-type energy analyzer (CLAM) in a VG Instruments, Inc. VG-ADES-500 system whose base pressure was 5×10^{-11} Torr. Before starting the measurements, surface superstructures were reconfirmed in the analysis chamber by low-energy electron diffraction. Samples were illuminated by monochromatic light ($h\nu$ was from 3.4 to 6.2 eV) produced by the emission of a deuterium lamp passed through a monochrometer (Jobin Yvon H-10UV). The stray light intensity was less than 5%, which is negligible when determining the ionization energy to within an accuracy of ± 0.01 eV. The total photoemitted current was determined by integrating the obtained photoemission spectrum. The vacuum chamber ion gauge was switched off during measurements in order to prevent stray electrons emitted by the gauge filament from reaching the electron analyzer. In addition photoemission spectrums were measured with the samples biased at -5 eV with respect to both the analyzer and the vacuum chamber. With this bias voltage excluded out of the measured spectrum range were the secondary electrons which were emitted from the inner walls of the analysis chamber due to cosmic ray. This applied voltage was small enough that the produced field did not change the measured ionization energy due to the "Schottky effect."[8] The photoemission yield (Y) was given by the total photoemission current divided by the photon intensity as measured independently by a calibrated photodiode. Following the theory of Ballantyne,[5] a plot of $Y^{1/3}(h\nu)^{2/3}$ versus $h\nu$ was fit to a straight line whose intersection with the abscissa gave a value for the ionization energy. Photoelectrons emitted by photons with energy near the threshold energy for photoemission deviated from Balantayne's theory. This was considered to originate from the emitted electrons from surface states. The existence of electrons in the surface states was confirmed by the method mentioned in Ref. 6, where a low-energy part of the photoemission-yield spectrum was found not to change when changing the contribution of valence electrons to the spectrum through a change in surface-band bending. The surface-band bending was changed for the "pinned"

GaAs(001) surfaces by varying the doping concentration.

Table I shows the measured ionization energies for samples with Ga (1×1), (4×6), $c(2 \times 8)$, $c(4 \times 4)$, and As (1×1) surface superstructures. Measured values were reproducible to within ± 0.01 eV for samples with the same surface superstructures. The measured ionization energy for the sample with the $c(2 \times 8)$ surface superstructure (5.35 eV) is in very good agreement with previous data (5.40 eV)[9] for which the surface superstructure was not explicitly described but a $c(2 \times 8)$ superstructure is reasonably supposed from the surface preparation method described there.

An outstanding feature of our observations is that the ionization energy varies by as much as 0.5 eV depending on the surface superstructure. This is not the case for the Si(111) surface where the same ionization energy was measured by photoemission-yield spectroscopy for both samples with (2×1) and (7×7) surface superstructures.[6] The ionization-energy variation for different superstructures of GaAs(001) is expected after a consideration of the ionic character of the GaAs surface. From a comparison of electron affinities, as determined by the "cut-off" energy of photoemitted electrons from the valence band, between several kinds of GaAs surface orientations, it was determined that a large contribution to the electron affinity arises from the surface dipole caused by the ionic character of the GaAs surfaces.[10] Note that the large energy difference of 0.5 eV observed for various GaAs(001) surface reconstructions in the present study is no less than the observed energy differences seen between different surface orientations. Furthermore, it has been reported that the range of observed surface dipole moments does not originate only from the ratio of Ga to As present at the surface but is also related to the surface atomic structure.[11] For two GaAs(110) surfaces with the same surface stoichiometry, different ionization energies were measured when different surface superstructures were present.[11] Therefore, our observed ionization energy dependence on the surface superstructure would suggest an atomic structure for each reconstructed surface.

It is interesting to correlate the present result to the surface As coverage for each surface structure. Figure 1 shows ionization energy as a function of surface As coverage. The As coverages were tentatively taken from those determined from Auger-electron-spectroscopy (AES) measurements for each surface superstructure.[1,12] It is noted that the ionization energy seems to vary in accordance with two trends: one trend is the increase in ionization energy observed as As coverage increases from the Ga (1×1) to the $c(2 \times 8)$ superstructure, and an opposing trend is seen as As coverage increases from the
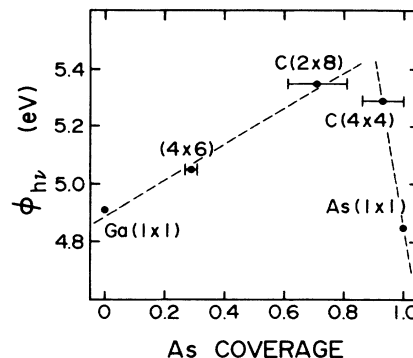

FIG. 1. The ionization energy (ϕ_{hv}) of the GaAs(001) surface as a function of surface As coverage. The As coverage was based upon the AES measurements in Refs. 1 and 12. The ionization energies are taken from those in Table I.

$c(4 \times 4)$ structure to the As (1×1) structure during which the ionization energy decreases.

First of all, it is found that the ionization energy of the Ga (1×1) surface (4.91 eV) is different from that of Ga metal (4.30 eV)[13] but is very close to that of the GaAs(111) surface (4.83 eV)[14] which is considered to be terminated completely by Ga atoms. This fact suggests that any positive contribution to the ionization energy arising from the dipole moment of ionic As—Ga bonding is minimized on this surface. Therefore, it may well be said that the positive dipole contribution to the ionization energy increases with increasing As coverage from zero to 0.14 eV, to 0.44 eV for the Ga (1×1), the (4×6), and the $c(2 \times 8)$ structures, respectively. Furthermore, this assumption leads to the idea that As coverage on the Ga-terminated surface monotonically increases as one moves from the Ga (1×1) to the $c(2 \times 8)$ surface. In fact, this idea is in good agreement with the facts that neither excess Ga nor excess As is found on the Ga-richer (4×6) surface[15] and on the As-richer $c(2 \times 8)$ surface.[16,17] However, it should be noted that very little is known about the atomic structure of the (4×6) surface reconstruction,[1,15,18,19] and that the 4×6 may not be a real surface structure but rather a superposition of diffracted beam for the 1×6 and 4×2 region.

According to the way of understanding for the first trend, the second trend is explained by excess As bonded with As atoms which reduces the positive dipole contribution to the ionization energy. Likewise, the surface is expected to be fully terminated with As atoms while the surface superstructure changes from the $c(2 \times 8)$ to the $c(4 \times 4)$ structure. In fact, this expectation is reasonably supported by the facts that As vacancies are observed on the $c(2 \times 8)$ surface,[17] while excess metallic As bonded with As atoms is found on the $c(4 \times 4)$ surface.[15] However, for the second trend, one should take into account a smoothing effect accompanied by a negative dipole moment observed for metals.[20,21] Finally, it is worth noting that, by taking into account the variation of the pinned Fermi energy for these surfaces,[1,7,15] these ionization energy dependencies are not inconsistent with the observed work-function dependence on surface superstructure

TABLE I. The ionization energy (ϕ_{hv}) for GaAs(001) surfaces with different surface superstructures. Measured values were reproducible to within ± 0.01 eV for the same sample.

Surface superstructure	Ga (1×1)	(4×6)	$c(2 \times 8)$	$c(4 \times 4)$	As (1×1)
ϕ_{hv} (eV)	4.91	5.05	5.35	5.29	4.85

which shows an even more complicated dependence.[4]

In summary, the ionization energies for various GaAs(001) surfaces were determined by photoemission-yield spectroscopy as a function of surface superstructure. The ionization energy changed by as much as 0.5 eV in accordance with different surface superstructures. The present result would give an important suggestion for an atomic model of the (4×6) surface reconstruction.

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