Photoemission-Based Photovoltage Probe of Semiconductor Surface and Interface Electronic Structure

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A saturation surface photovoltage is found to occur during ultraviolet photoemission at low temperatures ($T \sim 20$ K) on a variety of silicon (111) surfaces. Below ~ 50 K surface recombination becomes ineffective thereby allowing flat-band conditions to be achieved with mild uv irradiation. Temperature-dependent photoemission thereby provides a simple and direct method for determining band bending and barrier heights. Results for different silicon (111) surfaces and preparation conditions are discussed.

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Valence- and/or conduction-band offsets and potential gradients at semiconductor surfaces and interfaces are central to the understanding and controlling of a wide range of important semiconductor phenomena as well as electrical properties of semiconductor devices.[1] This includes not only ideal surfaces but heterostructure, semiconductor oxide, and metal-semiconductor interfaces. The most widely practiced spectroscopic methods used today for determining band bending and band offsets involve deconvoluting broad ($\sim \frac{1}{2}$ eV wide) surface and bulk core-level photoemission peaks[2,3] or examining photothresholds and performing adsorbate titration experiments to reference bulk band edges.[4,5] Each of these methods introduces its own uncertainties and limits one's ability to understand the systematics of a wide range of semiconductor interface phenomena.[6] Further, electrical measurements are not possible for some systems (e.g., free surfaces or thin layers) or practical in many types of experiments.

Here, we report a *temperature-dependent* surface photovoltage (SPV) effect that can be directly used to determine band bending for semiconductor systems. Previous studies have found enhanced SPV signals at lower temperatures[7,8] and have monitored small SPV offsets spectroscopically.[9] However, we show that at sufficiently low temperatures surface recombination processes freeze out and readily permit a saturation SPV to arise from mild uv irradiation. This effect has not been recognized nor observed previously. Such saturation photovoltages have only been observed with intense secondary optical illumination ($\sim 10^{19}$ photon/ cm-sec).[7,10] In our case, the use of uv photoemission to induce the SPV also provides new information not possible with ac-SPV methods[8,11,12] about the states involved in the SPV process. These results together with previous studies[7,9,10] suggest that this temperature-dependent uv-SPV saturation is a general phenomenon which can be used to determine band bending and band offsets in a wide range of semiconductor systems. Finally, this photoemission-based SPV measurement of band bending is not only very precise since it involves performing differential measurements at room and low temperatures, but can be performed with conventional, widely used uv photoemission equipment!

These measurements were performed in an ion-turbomolecular-titanium-sublimator-pumped ultrahigh-vacuum system having a base pressure of 4×10^{-11} Torr. The experimental system contains a cylindrical mirror analyzer (CMA) for Auger and ultraviolet photoemission spectroscopy (UPS), a three-grid low-energy electron-diffraction (LEED) optics, and a set of hemispherical deflection analyzers (2.5 cm diam) for high-resolution electron energy-loss measurements. A variety of samples and sample holders were used in these studies including Si disks, cleavage bars, and commercial wafers secured to sample holders as described elsewhere.[13-15] These sample holders were mounted to a cryostat so as to permit heating and cooling between 15 and 1400 K. Sample temperatures for the Si disks, wafers, and bars were measured via a Chromel-Alumel thermocouple mounted to the sample holder. Cooling of the samples was preceded by cooling of the cryostat which reduced system pressures below 2×10^{-11} Torr and virtually eliminated ambient contamination during cool down and measurements. Several different methods of surface preparation were employed involving sputter cleaning,[13] cleavage,[14] cleavage and thermal annealing,[16] laser annealing,[2] and thermal sublimation of a protective thermal oxide.[15] *p*-type Si having $(1, 1.3,$ and $3)\times10^{15}$ boron dopants/cm^2 and *n*-type Si having 10^{17} phosphorus dopants/cm^2 were studied.

In Fig. 1 we show uv photoemission spectra obtained from Si(111) 7×7 surfaces at 300 K for a *p*-type sample and at 20 K for an *n*-type sample. The zero in the kinetic energy scale represents the equilibrium, room-temperature Fermi-level location for both samples as determined by evaporation of a thick metal film on the sample or use of a sputter-cleaned, annealed metal surface. For both samples we observe a nearly uniform shift of the UPS spectra at low temperatures. This shift exponentially increases with decreasing temperature starting near 300 K and remains constant below ~ 50 K. For almost all the samples studied both the valence-band and surface-state features as

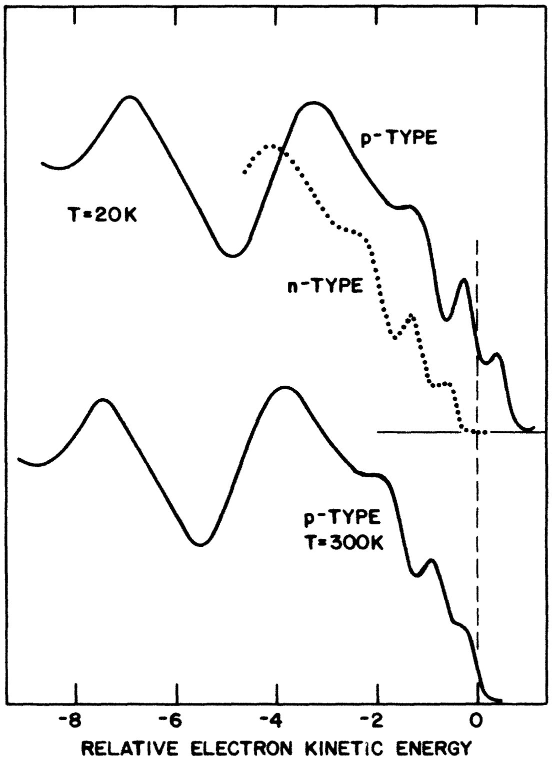

FIG. 1. Ultraviolet photoemission spectra ($h\nu = 21.2$ eV) of Si(111) 7×7 surfaces at $T = 300$ and 20 K. The n-type sample spectrum is not identical to the p-type spectra because of differences in sample orientation and overall spectrometer conditions. However, the temperature-dependent changes in the spectral features of the n-type sample are nearly identical to that observed for the p-type samples (see also Ref. 13).

well as the photoemission cutoffs (where measured) all shift by the same amount to within 0.05 eV. Such shifts are reproducibly observed for these and other silicon surfaces and, in principle, can arise from a number of physical phenomena such as sample charging, thermoelectric, or photovoltaic effects. In order to determine the origin of these shifts, several different samples, crystal surfaces, and sample dopings were examined. Potential experimental artifacts associated with our sample holder and sample contacts were evaluated by changing sample holders and contact metallurgy but were not found to effect the *differential* shifts observed in Fig. 1. At 20 K the same differential shifts were also found to exist with $h\nu - 40.8$ eV "filtered"[17] or unfiltered He discharge radiation, as well as with greatly attenuated ($\times 10^{-3}$) and visible-light-filtered $h\nu = 21.2$ eV radiation.[17] Sample-charging effects associated with unneutralized holes left during the photoexcitation process could account for the shift to lower kinetic energy observed for the n-doped samples, but fail to account for either the opposite shifts observed for the many p-type samples studied, or the specificity of this shift for different clean or adsorbate-covered surfaces. In Table I, we summarize the shifts we find at 20 K in the valence band and surface states for several of the samples and adsorbates studied, which we discuss later. We also list in Table I the previously deduced band bending for these systems. The correspondence between these shifts and the band bending leads us to propose a saturation SPV that arises at low temperatures which we discuss next.

In Fig. 2 (solid lines) we show a schematic energy-band diagram for a p-type semiconductor at room temperature and describe this temperature-dependent SPV effect. Here, the band bending V_s and barrier V_{bp} arises from the fixed positive charge at the surface (schematically shown by circled plus) which produces a depletion of free carriers (holes) in the surface region. This charge is not generally attributed to intrin-

TABLE I. Temperature-dependent shift in UPS spectra and reported band bending.

	Overall spectral shift (±0.02) (eV)	Band bending[a] at 300 K (eV)	Ref.
p-Si(111) 7×7 (excellent)	−0.65	−0.63 ±0.3	b
p-Si(111) 7×7 (average)	−0.4 to −0.6	−0.51	c
n-Si(111) 7×7 (excellent)	+0.46	+0.49	b
		+0.43	d
H_a-saturated p: Si(111)	−0.38	−0.31 to −0.43 i.e., 0.2 eV more than 7×7	e
p-Si(111) "1×1," laser annealed	−0.56	−0.5 to −0.63	c
2.5 Å Pd on p-Si(111) 7×7 (av)	−0.3	−0.30 (saturation V_{bp})	d
p-Si(111) 2×1, "best" cleave	−0.26	−0.32 ±0.8	f
p-Si(111) 2×1, av cleave	−0.20	−0.46 to −0.40	b
		−0.48	g

[a] − denotes bending of the bulk bands down; +, upwards.

[b] Reference 3.

[c] Reference 2.

[d] Reference 18.

[e] Reference 19.

[f] Reference 4.

[g] Reference 5.

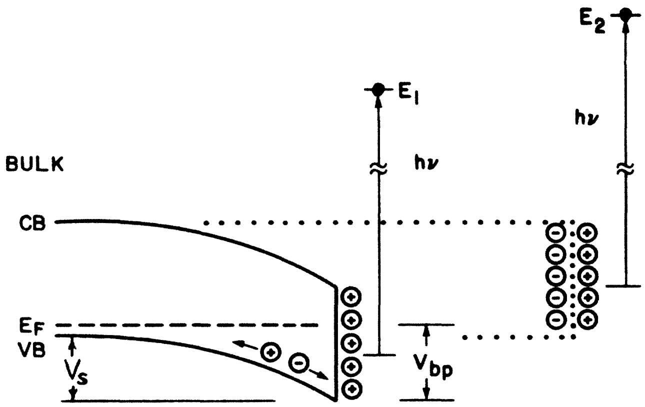

FIG. 2. Schematic band diagram for p-type Si at room temperature (solid lines) and with uv radiation at sufficiently low temperatures (dotted lines). The band bending at room temperature is denoted as V_s, and disappears at sufficiently low temperatures where photogenerated carriers produce a nonequilibrium emf which cancels the original band bending set up by the fixed surface charge. Photoemission from an equivalent surface state produces a photoelectron with energies E_1 and E_2 at room and low temperatures, respectively.

sic surface states, and photoionization of electrons from, for example, an intrinsic surface state indicated by the line produces electrons with kinetic energy E_1. A variety of photoinduced processes, including Auger emission and secondary electron scattering, creates electrons and holes in the samples denoted in Fig. 2 as the mobile charge in the depletion layer. At room temperature this charge recombines sufficiently fast not to alter the equilibrium electrostatic potential in the surface region. Our findings show that at sufficiently low temperatures the reduced surface recombination allows this charge to set up a nonequilibrium emf which cancels the band bending. This can most simply be viewed as a self-limiting process whereby the surface band bending is needed to separate or trap the mobile carriers that produce this emf. This compensating emf is schematically represented in Fig. 2 as the negative charge which balances the fixed positive charge. As a result of this induced emf, the photoemission spectrum of the surface state observed at room temperature has now shifted from energy E_1 to energy E_2 by V_s. This differential shift thereby represents the band bending (or surface potential) at room temperature and differs from the barrier height V_{bp} by the position of the Fermi level above the valence-band edge. We note a similar shift in the leading edge of the valence band has also been observed in recent time-resolved UPS studies of GaAs.[20] In this case the UPS spectrum is obtained immediately after intense pulsed uv irradiation occurs. In our case, we exploit the temperature dependence of the recombination processes to achieve a saturation SPV with mild, continuous irradiation. We avoid intense irradiation which can strongly alter charge and carrier distributions in the space-charge layer.[11,21]

The simplified description presented above ignores complications such as potential gradients associated with diffusing holes and electrons, i.e., the Dember effect,[21] as well as the expected temperature-dependent change of the bulk E_F which is discussed later. A small Dember potential is not unexpected since our SPV arises from the freezeout of surface recombination processes and not necessarily by the production of large current densities of holes or electrons. It also appears that the photon fluxes used for UPS ($\sim 10^{14}$–10^{17} photons/cm^2-sec) produce a sufficient supply of charge carriers to "compensate" the fixed surface charge at low temperatures with any excess carriers being neutralized by bulk recombination processes. We find that surface-recombination "freezeout" is complete by 50 K, and at 20 K variations in the uv intensity by 3 orders of magnitude still maintain the saturated SPV! The temperature dependence of the band-bending shifts for p-Si(111) 7×7, shows Arrhenius behavior characterized by an activation energy of ~ 20 meV between 300 and 100 K and ~ 0.5 meV below. Presumably these activation energies are related to the surface and bulk recombination processes, respectively.

The use of UPS in generating this saturation SPV further allows us to probe the changes arising in the surface electronic structure that produce this SPV. One immediately questions whether the temperature-dependent spectral changes in the intrinsic surface states for the Si(111) 7×7 surface[13] are a direct result of the SPV. We do not believe this to be the case since we have not observed such temperature-dependent UPS spectral changes for any of the other Si(111) surfaces listed in Table I. Further, the temperature-dependent spectral changes of Si(111) 7×7 are nearly identical for both n- and p-doped samples even though opposite SPV's arise. If a simple filling or emptying of states near E_F were involved in the SPV, we would expect the leading edge of the highest-lying surface state of Si(111) 7×7 to shift to higher or lower energies, respectively. This is not observed and this edge shifts with all the other surface-state features, except as discussed later for the metal/Si systems. The saturation SPV-induced changes in the UPS spectra for the other clean surfaces are generally very small and not specific to any particular surface states or energy range. We thus see no evidence for discrete trap states which could play a role in the SPV effect. The apparent absence of the temperature dependence of the bulk Fermi level from our SPV shift implies a Fermi-level position in or below the depletion depth which is not temperature dependent (possibly a result of the nonequilibrium nature of the SPV process).

In considering the results in Table I in more detail, we find the strongest disagreement in band bending for the cleaved Si(111) 2×1 surface. This is not surprising considering the possibility of mixed cleavage domains, surface steps, or atomic scale microstructure.[22] Our best value is considered to be from a cleaved sample showing negligible electronic transitions below the surface-state band transition (see Ref. 14). However, the differences between this "good" cleave band bending and that observed for "poorer" cleaves (still single domain) corresponds identically to that found previously.[3] The variations of band bending we find for Si(111) 7×7 are also consistent with those found earlier,[2,3,18] the larger values being found on oxide sublimation-cleaned samples. We also find the same large values on our best sputter-cleaned/annealed *p*-type samples. The lower values of band bending we find for other 7×7's on *p*-type Si are more typical of sputter-cleaned sample and can be related to poorer surface perfection (i.e., higher diffuse elastic scattering in LEED and broader surface states) as well as, in some cases, to "incipient" residual carbon contamination. Carbon contamination arising from improper cleaning procedures also reduced the band bending of the *n*-type samples by up to 0.4 eV! These results confirm that different sample processing conditions can,[23] but need not, modify semiconductor surface properties.

We expect this temperature-dependent photoemission-based SPV method to be applicable to a wide range of systems including adsorbates and metal layers on semiconductors as well as semiconducting heterojunctions. One possible problem of this SPV method for other systems is that the activation energy for free-carrier recombination processes at the surface or interface may be smaller than found here and thereby prevent a saturated SPV. Considering other results[7–12] we doubt this to be the case. Nevertheless, this situation can be experimentally evaluated from the temperature dependence of the SPV. Finally, an important and novel feature of such photoemission-based SPV measurements is that the spatial localization of bulk and surface states within the space-charge layer can be determined by the differences in SPV that these states exhibit. Of course, these differences will only be measurable for narrow depletion layers such as occur in very heavily doped surfaces or interfaces, or for metal layers on semiconductors. In fact, the spectroscopic difference between the SPV of the valence band and the surface states was found to be the largest for Pd or Au on Si(111).

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