

Microscopic surface photovoltage spectroscopy

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We present a microscopic surface photovoltage spectroscopy method. It is based on a tunable illumination system combined with a kelvin probe force microscope, which measures the contact potential difference between a sample surface and a tip of an atomic force microscope. By measuring the contact potential difference as a function of illumination wavelength, the whole surface photovoltage spectrum of a semiconductor sample is obtained with submicrometer spatial resolution. This resolution can be as high as 100 nm, in regions where the minority carrier transport is controlled by drift rather than by diffusion. © 2002 American Institute of Physics.

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Surface photovoltage (SPV) is a well-established technique for the characterization of semiconductors, which is based on analyzing illumination-induced changes in the semiconductor work function, in a contactless, nondestructive manner. For almost five decades, it has been used as an extensive source of surface and bulk information on various semiconductors and semiconductor interfaces.¹ These research efforts have shed light on many scientifically and technologically important questions, especially in the areas of metal–semiconductor interfaces, semiconductor–insulator states, surface state passivation, bulk defects, and minority carrier lifetime and diffusion length. To date, almost all the SPV related techniques (apart from several preliminary reports mentioned later) have a common significant drawback: *they do not have high spatial resolution.*

Scanning probe microscopy has enabled imaging of semiconductor electronic properties with unprecedented spatial resolution. Both scanning tunneling microscopy (STM),² and atomic force microscopy (AFM)³ have been modified to obtain high-resolution maps of the electric surface potential distribution. The applications of the STM are limited to conductive samples, and suffer from additional drawbacks described in Ref. 2. With the development of the kelvin probe force microscopy (KPFM)³ this major disadvantage was overcome, because forces are measured instead of tunneling currents.

The KPFM has found many diverse applications in recent years. It has been used to measure surface electronic properties like: charges,⁴ dielectric constants,⁵ photovoltage,⁵ and electrical potential distribution across operating semiconductor devices.⁶ In this work we use KPFM in order to measure SPV with high spatial resolution. The method is based on a tunable illumination system combined with a KPFM, which measures the contact potential difference (CPD) between a sample surface and an AFM tip. By conducting measurements on cleaved GaP *pn* junctions it is shown that the lateral resolution of the technique can be as high as 100 nm.

The system is schematically described in Fig. 1. It includes a light source (150 W Xenon arc lamp), and an imag-

ing monochromator (Scienceteh Inc.) coupled through an optical fiber to the KPFM system. The optical fiber is brought to a distance of tens of microns from the sample using a micrometric translation stage. The light spot on the sample surface is several hundreds of microns in diameter, and the optical power at the fiber output is tens of microwatts (wavelength dependent). The use of an arc-lamp imaging-monochromator illumination system is needed in order to maximize the light intensity reaching the sample; an imaging monochromator has a very high quality toroidal optics, with an imaging spot size of around 50 μm at the exit slit.

The KPFM is based on a commercial AFM (Autoprobe CP, Thermomicroscopes, Inc.) operating in the noncontact mode. An alternating voltage $V_{ac} \sin(\omega t)$ at a frequency of around 20 kHz was applied to the cantilever in order to induce an alternating electrostatic force between the tip and the sample. The CPD between the tip and the sample surface was measured in the conventional way by nullifying the output signal of a lock-in amplifier, which measures the electrostatic force at the frequency ω .^{7,8}

The GaP samples used in this study (Elma Inc.) were grown by liquid phase epitaxy. They consisted of *p/n⁺/n* structures of 20- μm -thick Zn doped GaP $p \approx 5 \times 10^{17} \text{ cm}^{-3}$ layer on top of a 40- μm -thick *n*-type layer grown on a GaP *n*-type substrate. Ohmic contacts were formed using evaporation of Ni/Ga/Au/Ni/Au for the *n*-type layers, and Pd/Zn/Pd for the *p*-type layers. The measurements were carried out in two main configurations: (a) measurements on a cleaved *pn* junction, and (b) measurements on the *p*-GaP surface; in this case the *pn* junction is located 20 μm below the surface.

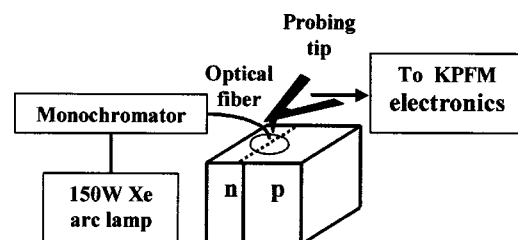


FIG. 1. Schematic diagram of the μSPS measurement setup.

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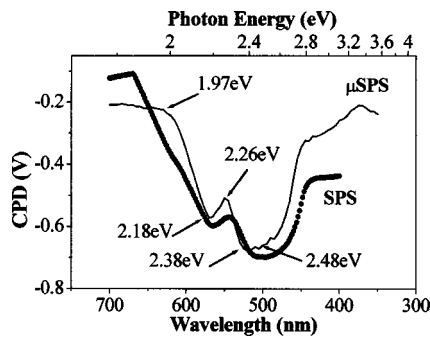


FIG. 2. GaP spectra measured on the *p*-GaP surface using the μ SPS method (solid line) and by conventional SPS method (dotted line).

Figure 2 shows two photovoltage spectra measured by the microscopic method, hereafter called microscopic surface photovoltage spectroscopy (μ SPS) (solid line), and using a conventional macroscopic surface photovoltage spectroscopy (SPS) system¹ (dotted line). Although the spectra are not identical (the sharp change at an energy of 1.85 eV in the SPS spectrum is due to filter exchange in the illumination system), it is clear from the figure that the general behavior is similar. The different features occur at the same wavelengths; the difference in the photovoltage magnitude is due to the different illumination systems used in the μ SPS and SPS systems.

Both spectra contain features related to the *n* layer, the buried *pn* junction and the top *p*-type layer. The photovoltage change at 1.97 eV is the onset of the decrease in the buried *pn* junction built-in voltage, which can be explained in the following way. The measured GaP structure includes two space charge regions: one at the surface (the *p*-GaP surface depletion region) and the second is the buried *pn* junction. Under illumination, light is absorbed in the two space charge regions (SCRs); this results in a decrease of the built-in voltage in both junctions due to the photovoltaic effect. Since the substrate is grounded, and due to the fact that the band flattening in the *pn* junction is much larger than the one in the surface SCR (due to larger built in voltage), the measured SPV is governed by the buried junction and thus it is negative. This decrease in the photovoltage continues until an energy of 2.38 eV. At this photon energy the spectrum slope changes because with increasing energy, less photons reach the buried junction and the CPD decreases back to its dark value. The increase in photovoltage between energies of 2.18–2.26 eV is attributed to the indirect band-to-band transition at the surface of the top *p* layer, which reduces the surface-band bending and increases the CPD. The change in the spectrum slope at 2.79 eV is due to a direct band-to-band transition at the surface *p* layer. For a detailed description of all the mechanisms of SPV change see Ref. 1.

μ SPS measurements conducted at many different points on the *p*-GaP surface resulted in identical spectra. Thus, in order to demonstrate the spatial resolution of the μ SPS technique, a series of spectra were measured on the surface of an air-cleaved *pn* junction. Figure 3(a) shows a KPFM image measured in the dark on the cleaved *pn* junction. Such images have been analyzed by us in detail in the past.⁹ In ideal (surface states free) cleaved structures, the region with the higher CPD is the *p* side of the junction since it has a higher

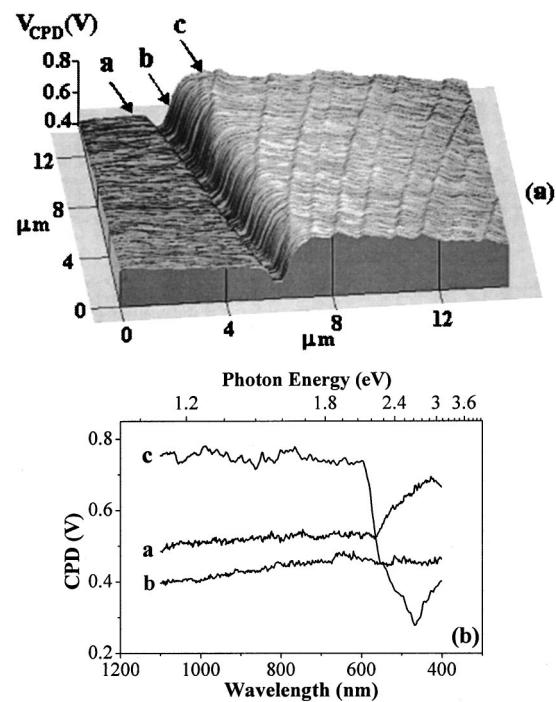


FIG. 3. (a) KPFM image of the cleared GaP *pn* junction. The arrows show the location where the μ SPS spectra presented in (b). The distance is measured from the estimated location of the surface metallurgical junction. (I) 2.4 μ m (*p* side), (II) at the metallurgical junction, and (III) 3.4 μ m (*n* side).

work function than the *n* side. However, in Fig. 3(a), the region with the higher CPD is the *n*-GaP due to reasons explained later.

Figure 3(b) shows three μ SPS spectra measured at three different distances [exact locations shown in Fig. 3(a)] from the surface metallurgical junction of the *pn* diode: (a) 2.4 μ m (*p* side), (b) at the metallurgical junction, and (c) 3.4 μ m (*n* side). It is observed that the spectrum measured on the “*n* side” of the junction (curve a in Fig. 3) shows a *p*-type behavior (CPD increases with increasing photon energy at the band gap energy). Similarly the “*p* side” of the junction shows a *n*-type behavior. This discrepancy is most probably due to inversion of the GaP surface which causes the *p*(*n*) side of the junction to become *n*(*p*) on the surface; this “inverts” the CPD image [Fig. 3(a)]. This is supported by the following measurement: when the cleaved *pn* junction is illuminated using superband gap energy laser (404 nm gallium nitride laser, intensity of 3.5 mW), the energy bands at the surface SCR are flattened (not to flatband conditions); this causes the *pn* junction to invert back to a typical *pn* junction image with the work function of the *p* side higher than that of the *n* side. In summary, the μ SPS has enabled us to identify the correct doping type of the two sides of the junction. This is one of the advantages of the μ SPS method.

The spectrum measured at the middle of the *pn* junction [curve b of Fig. 3(b)] shows no SPV response. The SPV is proportional to the minority carrier concentration; in the space charge region of the *pn* junction the built-in electric field sweeps both electrons and holes away from the junction resulting in a very small (immeasurable) SPV. The SCRs of the *pn* junction should not be confused with the surface space charge regions. These SCRs sweep the minority carriers towards the surface thus inducing large SPV.

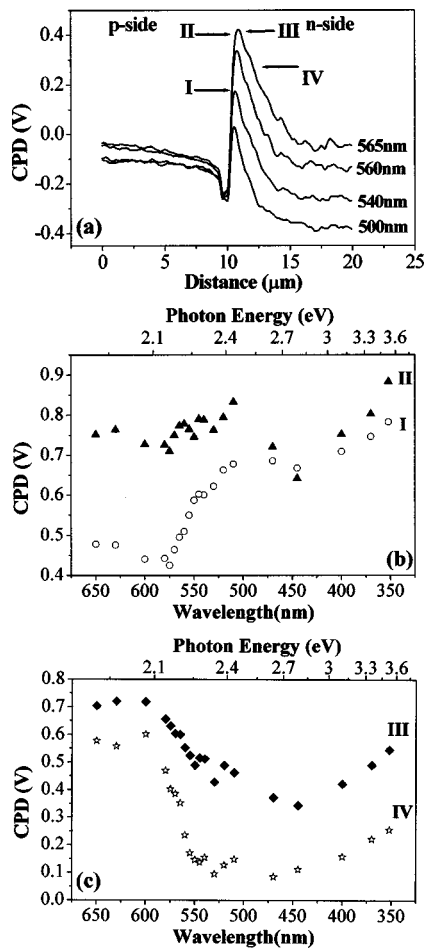


FIG. 4. (a) CPD line scans measured across GaP *pn* junction excited with different wavelengths. The curved regions demonstrate the minority carrier diffusion; for a quantitative analysis see Ref. 9. (b) μSPS measured at distances of: (I) \circ 0.06 μm , and (II) \blacktriangle 0.17 μm from the middle of the depletion region. (c) μSPS measured at distances of: (III) \blacklozenge 0.82 μm , and (IV) \star 2.4 μm from the middle of the depletion region.

The spatial resolution of the μSPS can be estimated by comparing spectra measured at different distances from one another like the data presented in Fig. 3(b). Another way is by measuring SPV images (on the cleaved *pn* junction) at several wavelengths, as shown in Fig. 4(a), and transforming the data to surface photovoltage spectra. The curved region [present in all wavelengths in Fig. 4(a), on the right side of the *pn* junction], is due to the minority carrier diffusion towards the junction as described in our previous work.¹⁰ A series of surface photovoltage spectra extracted in this way are presented in Figs. 4(b) and 4(c). Figure 4(b) shows two spectra measured at distances of (I) 0.06 μm , and (II) 0.17 μm , and Fig. 4(c) at distances of (III) 0.82 μm , and (IV) 2.4 μm from the *pn* metallurgical junction.

The two spectra in Fig. 4(b), which were measured at a distance of 110 nm apart, are clearly different. In spectrum I (which is measured at the middle of the depletion region) the onset of the change in the CPD is at an energy of 2.16 eV, and the spectrum then shows a “*p*-type behavior,” i.e., an increase of 250 mV in the CPD due to superband gap illumination. On the contrary, spectrum II (measured 110 nm from spectrum I towards the *n*-type region) changes much less as a function of photon energy.

In comparison, the two spectra in Fig. 4(c), show a similar photovoltage difference, but they were measured at a distance of 1.6 μm apart. This is due to the fact that spectra I and II were measured in the *pn* junction SCR where the minority carrier transport is controlled by drift and not by diffusion (as in the case of curves III and IV). Thus, we conclude that high spatial resolution (~ 100 nm) can be achieved if μSPS are measured in regions where the minority carrier transport is dominated by drift. In other regions the resolution is on the order of the minority carrier diffusion length, 1–2 μm in the case of GaP, as shown by the curved regions in Fig. 4(a).

In conclusion, a high spatial resolution SPS method was demonstrated using a system that combines a KPFM and a tunable illumination source. It was shown that the spatial resolution depends on the minority carriers transport mechanism. This method may be utilized in SPV related research and applications that were not possible until now like: SPV spectra of single (submicron) electronic devices, SPV mapping of differently processed wafer regions, study of lateral inhomogeneity in quantum devices, single quantum dot photovoltage spectroscopy and more.

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