Surface photovoltage spectroscopy of semiconductor structures: at the crossroads of physics, chemistry and electrical engineering

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The possibility of obtaining a detailed picture of the electronic structure makes surface photovoltage spectroscopy (SPS) eminently suitable for bridging the gap between the chemical, physical, optical and electrical properties of semiconductors. In SPS, changes in band bending (both at the free semiconductor surface and at buried interfaces) are monitored as a function of external illumination. Surface photovoltage spectroscopy can provide detailed, quantitative information on bulk properties (e.g. bandgap and type, carrier diffusion length and lifetime) and can be used for complete construction of surface and interface band diagrams, including the measurement of energy levels in quantum structures. A particular strength is that a comprehensive analysis of surface and bulk defect state distributions and properties is made possible. Measurements using SPS are contactless and non-destructive. In addition, they can be performed both in situ and ex situ, at any reasonable temperature, on any semiconducting material, at any ambient and at any lateral resolution down to the atomic scale. This review starts with an overview of SPS-related surface and interface theory, describes the SPS experimental set-up and presents applications for surface and interface characterization of a wide variety of materials and structures, cross-correlating them with other methodologies. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

The surface photovoltage (SPV) method is a well-established contactless technique for semiconductor characterization that relies on analysing illumination-induced changes in the surface voltage. Starting from the pioneering work of Brattain and Bardeen in the early 1950s,1 it has been used in the last five decades as an extensive source of surface and bulk information on various semiconductors and semiconductor interfaces. Simultaneously, it has evolved considerably in terms of both methods for data analysis and the performance of experimental tools.

In previous work we have provided a comprehensive, tutorial treatise of surface photovoltage phenomena.2 In this review article we concentrate on one specific variant of the SPV method: surface photovoltage spectroscopy (SPS), in which changes in the surface voltage are monitored as a function of incident photon energy. The history of SPS begins with the systematic research on the effects of subbandgap illumination on the surface voltage, performed by Gatos, Lagowski and Balestra in the early 1970s.3 These researchers realized that they had invented a powerful tool for surface state characterization and also coined the term SPS. Throughout much of the 1970s and 1980s SPS was popularized and applied successfully to a great variety of semiconductors and semiconductor surfaces, notably by Brillson,4 Mönch,6 Lüth8 and subsequently many others. Starting in the mid-1990s, Shapira’s group, and more recently Pollak’s group, have systematically applied SPS for quantitative studies of various semiconductor interfaces and heterostructures,10–13 including actual device structures.14–16

The present article is intended to provide a brief overview of the current state of the art in SPS research and applications. Following this brief introduction of the technique and its uses, the second section is devoted to a synopsis of surface and interface theory necessary for understanding the inner workings of SPS. We have tried to keep the theory as phenomenological and intuitive as possible, so that the reader may grasp the essential capabilities and achievements of SPS without being mired in formal and mathematical detail. The third section is devoted to a survey of SPV measuring tools. In the fourth section, we explain how SPS is applied in practice to the study of surface and interface properties. We bring examples ranging from basic research to industrial applications and from a wide variety of materials and structures, including bulk materials, thin films, nano- and quantum structures and...
(opto) electronic device structures. In the fifth and final section we show how the cross-correlation of SPS with other optoelectronic techniques of characterization on the one hand and traditional surface science techniques on the other hand provides a powerful tool for linking the physics, chemistry and electrical performance of semiconductors.

OVERVIEW OF SPS THEORY

Electronic structure of surfaces

Our overview of theory starts by recapitulating the basic electrical properties of semiconductor surfaces. This summary is loosely based on our SPV treatise and on the fine books by Many et al., Mönch, Lüth and Sze.

In general, a surface is defined as a boundary of media with different physical properties. The surface between a semiconductor and vacuum or gas often is referred to as a 'free surface' and the surface between a semiconductor and another solid usually is referred to as an 'interface'.

The periodic structure of an ideal crystalline semiconductor results in the appearance of allowed energy bands separated by forbidden energy gaps. The termination of the periodic structure of a semiconductor at its free surface may form surface-localized electronic states within the semiconductor bandgap and/or a double layer of charge, known as a surface dipole. The formation of surface- and interface-localized states typically involves additional, more complex phenomena than the symmetry-breaking lattice termination, such as: dangling bonds, the formation of surface atoms with no upper atom to bind to; surface reconstruction or relaxation, i.e. a change in the position and/or chemical bonding configuration of surface atoms that minimizes the surface energy; steps and kinks at the surface; impurity atoms adsorbed on the surface; etc.

The appearance of surface-localized states induces charge transfer between bulk and surface in order to establish thermal equilibrium between the two. The free carrier density in the vicinity of the surface therefore deviates from its equilibrium value in the bulk. This results in a surface space–charge region (SCR), which is electrically non-neutral, implying a non-zero electric field in it and therefore a potential drop across it. Thus, even under equilibrium conditions the surface potential \( V_s \) is different from the electric potential far away in the bulk. As a specific example, consider an n-type semiconductor with a depleted surface, i.e. one where the majority carriers (electrons) have been trapped in surface states such that their concentration in the vicinity of the surface is smaller than its equilibrium value but larger than that of the minority carriers (holes). The potential drop across the SCR is manifest by the bending of the semiconductor bands, which is such that electrons are repelled from the surface and holes are attracted to it, due to the trapped surface electrons. We note that, by definition, the energy band edge is lower the higher the electrical potential is, so that a positive \( V_s \) corresponds to downward-bent bands.

In addition to surface states, another important phenomenon associated with a semiconductor surface is the surface dipole \( \Delta \phi_s \). The surface barrier is usually characterized by means of the electron affinity \( \chi \), defined as the energy needed to release an electron from the conduction band into a vacuum. At a real semiconductor surface or interface, an effective surface barrier may be determined by additional microscopic dipole contributions due to, for example, reconstruction, stoichiometry changes or adsorption.

The difference between the effect of surface states and the surface dipole on the semiconductor band diagram is best illustrated by the concept of a local vacuum level \( E_l \) defined as the energy of an electron at a given point if it is at rest and free from the influence of the crystal potential (which determines the underlying band structure) but not from macroscopic potentials, e.g. those due to the electric field at a SCR. The local vacuum level therefore must follow any changes in the electric potential along the sample. The electron affinity then is defined as \( \chi = E_l - E_C \), where \( E_C \) denotes the conduction band energy. At the surface, the effective electron affinity \( \chi' \) may differ from that of the bulk due to the various surface dipole effects discussed above. These quantities are illustrated in the complete schematic band diagram of a semiconductor surface SCR at equilibrium, shown in Fig. 1(a). This figure also shows the semiconductor surface work function \( \phi_s \) defined as the energy separation between the Fermi level \( E_F \) and the local vacuum level at the surface.

The surface photovoltaic effect

Generally, the photovoltaic effect comprises an illumination-induced change in the equilibrium potential distribution and is typically the result of some charge transfer and/or redistribution within the device due to the incident illumination. A specific variant of the photovoltaic effect is the surface photovoltaic effect, which is at the centre of this text. It is important to note that the formation of a SPV occurs only if carrier generation per se is followed by net charge redistribution. Normally, no significant driving force for such redistribution is found beyond the SCR and the underlying bulk remains quasi-neutral. Only in the presence of significantly non-uniform generation or recombination may this assumption break down (this is known as the Dember potential and is not discussed further here). Thus, we are interested primarily in the surface SCR.

The SPV mechanism depends strongly on whether the incident photon energy is super-bandgap or sub-bandgap, i.e. on the dominant carrier excitation mechanism. All mechanisms are demonstrated below for a depleted n-type surface. The dominant mechanism by which super-bandgap illumination results in SPV generation is shown in Fig. 1(b). The electric field in the SCR causes excess electrons to be swept away from the surface and excess holes to be swept towards it. This serves to reduce the density of surface-trapped electrons and decreases the band-bending. In a second mechanism, shown in Fig. 1(c), either electrons or holes are preferentially trapped at surface defects. This effectively charges the surface and thus modifies the surface potential. This second mechanism is usually apparent in bulk samples only if the equilibrium surface band-bending is fairly small, but increases in importance in polycrystalline material with decreasing crystallite size because of an increasing surface to volume ratio.
The most common mechanism for sub-bandgap SPV involves the direct modification of the surface charge, and hence potential, by excitation of trapped carriers, as shown in Fig. 1(d). Illumination by photons with energy $h\nu > E_t - E_c$ may produce electron transitions from a surface state at an energy $E_t$ into the conduction band, where they are swept quickly to the semiconductor bulk by means of the surface electric field. Hence, the negative surface charge is reduced and the band-bending is decreased. Conversely, illumination by photons with energy $h\nu > E_t - E_v$ may produce electron transitions from the valence band into a surface state situated at an energy $E_t$ above the valence band maximum $E_v$ (which are equivalent to hole transitions from the surface state to the valence band). Such transitions increase the surface negative charge and therefore the surface band-bending. For the SPV to develop in this case it is necessary to have a significant diffusion of the excess holes into the bulk and/or a significant recombination of electrons and holes inside the SCR, because there is no field-assisted driving force of holes into the bulk. Other mechanisms for sub-bandgap SPV are based on band-to-band transitions, made possible with sub-bandgap photon energies. One notable example, shown in Fig. 1(e), is the Franz–Keldysh effect, in which sub-bandgap photons excite band-to-band transitions in a sufficiently large electric field via photon-assisted tunnelling. The photon energy under such circumstances is typically close to $E_g$.

We note that because the optically induced SPV-generating electron transitions take place against a background of thermal transitions, the magnitude of the SPV effect generally increases with decreasing temperature, for both super-bandgap and sub-bandgap illumination.2,3
Sensitivity to buried interfaces

The preceding discussion has been devoted solely to a study of semi-infinite, uniform bulk samples. However, actual semiconductor samples may be thin, i.e. not much larger than the diffusion length and/or the absorption length, so that excess carriers may be present near their back part as well. Samples also may have a multilayer structure that has several buried interfaces due to homojunctions and heterojunctions in the structure.

At first glance, interfaces that are buried deep enough into the sample may seem unable to contribute to the measured SPV signal, due to screening by a thick-enough quasi-neutral region. However, this statement is erroneous. To understand why, let us consider a semiconductor sample comprising a semiconducting film grown on a semiconducting bulk substrate that may have different material parameters. A schematic typical band line-up of such a structure in the dark (solid curve) and under illumination (dashed curve) is shown in Fig. 2.10 There are two SCRs in such a sample (not including the back contact, assumed to be ohmic): an interface SCR (between the substrate and the film) and a surface SCR (between the film and the ambient). Figure 2 clearly shows that optical absorption in any non-neutral region present within the sample (be it band-to-band or defect-state-to-band) may contribute to the measured SPV signal because the potential of the free surface is linked to any other illuminated region, no matter how deep within the sample, because the energy bands are connected serially. Thus, the sensitivity of SPV measurements to a certain region in the semiconductor is limited only by the absorption length of the photons, i.e. by the possibility of introducing an excess of free carriers in the region of interest.

The sensitivity of SPV measurements to buried interfaces is underscored by the two different SPV scenarios shown in Fig. 2: in both, the SPV is produced by changes in the band-bending of both the interface and the surface SCRs. However, as evident from the surface position of $E_l$, in one case the surface-related SPV dominates, whereas in the other case the interface-related SPV dominates. Thus, even though in SPV the experimentally measured quantity is strictly a surface quantity and as a result the technique is highly surface sensitive, it is also sensitive to photovoltaic effects whose physical origin has nothing to do with the surface. Therefore, by proper design and interpretation of experiments SPV may be used effectively to gain information about various semiconductor interface and bulk properties, in addition to semiconductor surface properties.

EXPERIMENTAL SET-UP

The SPV measurements are non-trivial because the surface potential is a built-in potential rather than an external potential. In other words, the surface potential is not equal to the difference in Fermi levels between the front and back surfaces and therefore cannot be measured simply with some form of voltmeter. Moreover, in the case of a free surface the application of any contact to indirect electrical measurements of the built-in voltage (e.g. current–voltage or capacitance–voltage analyses) invariably will alter the surface properties and hence the quantity under measurement. Consequently, many elaborate techniques for measuring the surface potential (or at least changes of it) without applying a direct electrical contact have emerged.

![Figure 2. Band line-up of a typical thin-film structure in the dark (solid curve) and under illumination (dashed curve), where the dominating contribution to the SPV is from: (a) the interface SCR; (b) the surface SCR. (After Ref. 2, reproduced by permission of Elsevier Science.)](image-url)
The Kelvin probe

An important key to some techniques of SPV measurement is found by re-examining Fig. 1(a). Because, in the absence of photochemical activity, the surface dipole is illumination insensitive, any change in the surface band-bending $eV_s$ causes a change of equal magnitude in the surface work function $W_s$. Therefore, under such conditions a measurement of work function changes is completely equivalent to a direct SPV measurement (in absolute value terms).

One of the oldest techniques for measuring the work function difference between two materials is by forming a parallel plate capacitor. For simplicity, this is demonstrated in Fig. 3(a) for two metals. Prior to connection [Fig. 3(a)] the metals are electrically neutral—no macroscopic electrical fields arise—and the two metals share the same local vacuum level. Upon short-circuiting the metals [Fig. 3(b)] charge must flow from the metal with smaller work function to the metal with larger work function until equilibration of the Fermi levels is achieved. As in any parallel plate capacitor, this charge transfer results in an electric field in the gap between the two plates and a drop in the local vacuum level across this gap. The potential energy drop is equal to the difference in the work functions of the two metals and is usually known as the contact potential difference (CPD).\(^{17,19}\)

Lord Kelvin suggested that the CPD may be measured directly by a null method: when an external d.c. bias, equal and opposite to the CPD, is applied to the capacitor [Fig. 3(c)], the Fermi levels on both metals differ by $eV_{CPD}$, just as in the isolated case. No charge exchange between the metals need take place and the capacitor is discharged. Hence, in order to determine the CPD it suffices to determine the applied bias that discharges the capacitor, even if neither capacitor charge nor capacitance is known. This type of arrangement is known as the Kelvin probe, after its inventor. In practice, most modern Kelvin probes rely on a periodically vibrated plate brought in proximity to the sample surface, such that a steady-state a.c. current develops in the effective a.c. capacitor formed.\(^{25}\) This current can be zero if, and only if, the capacitor is discharged. Thus, the CPD may be found easily, even automatically, by determining the d.c. bias for which the external a.c. current is nullified.

The metal–insulator–semiconductor approach

An alternative approach, in which the SPV is measured directly, utilizes a metal–insulator–semiconductor (MIS) structure. Assume that after equilibrium is established a MIS capacitor is brought into open-circuit mode by disconnecting its two terminals. If illumination now is applied to the capacitor, $V_s$ may change due to the photovoltaic effect. The change in $V_s$ must produce an equal change in the voltage measurable between the two capacitor terminals. Thus, the SPV at the semiconductor/insulator interface in a MIS structure can be found by measuring the photoinduced (external) voltage change between the MIS capacitor terminals.\(^{26}\) This approach is readily applicable to the study of a free semiconductor surface by placing a static metallic grid in proximity to the sample, with the air or vacuum gap functioning as the insulator; and using chopped illumination in conjunction with lock-in detection of the ensuing SPV signal.

The different physical principles behind the Kelvin probe and MIS approaches result in several relative strengths and weaknesses, which make the method of choice application dependent. In a nutshell, the Kelvin probe is more suitable for following phenomena with large time constants (in particular surface states with long relaxation times), does not perturb the true band-bending of the free surface and the extra information afforded by the work function is extremely useful in experiments involving surface chemistry and/or film deposition. The MIS technique is more suitable for following fast relaxation phenomena, allows for a systematic modification of the surface band-bending in the dark as an extra degree of freedom and alleviates the need for

Figure 3. Schematic band diagram of a parallel plate capacitor formed from two different metals, with the two plates isolated (a), short-circuited (b) or connected through a d.c. bias equal and opposite to the contact potential difference (c). (After Ref. 2, reproduced by permission of Elsevier Science.)
an ohmic back contact (which is a must in Kelvin probe measurements).2

**Scanning SPV measurements**

Both Kelvin probes and MIS structures may be employed also in a scanning mode, which allows for recording lateral variations in the SPV by scanning a small probe27 or a well-focused light beam,26 respectively, across the surface. Both approaches are typically limited to a lateral resolution roughly of the order of ~1 μm.26,27

Applications of SPV requiring an even finer lateral resolution rely on two high-resolution techniques for topographic mapping of surfaces that have emerged in the 1980s:28 scanning tunnelling microscopy (STM), based on sensing the tunnelling current between a tip and the sample; and atomic force microscopy (AFM), based on sensing the deflection of a tip due to tip–sample forces. In the early 1990s both STM29 and AFM30 have been shown to be useful also for SPV measurements, opening new horizons for SPV mapping with a resolution previously unknown. Because SPV measurements with either STM or AFM have yet to be applied in a spectroscopic mode, we shall not dwell on this issue further here. However, the recent STM- and AFM-based SPV research of the groups of Haase31 and Rosenwaks,32 respectively, clearly demonstrates the potential of these tools.

**The SPS set-up**

Having discussed the means of measuring the SPV signal, we now briefly address the complete generic SPS set-up, a schematic view of which is given in Fig. 4. The sample under study is typically placed inside a metallic box, which serves as both a dark box and a Faraday cage. This box must be such that it effectively includes the probe, be it a vibrating metal plate (i.e. a Kelvin probe), a static one (i.e. part of an MIS-structure set-up) or an AFM or STM tip.

Clearly, for spectroscopic purposes one needs to generate the SPV signal using a broadly tunable light source. The default choice therefore would be the use of a ‘white light’ source in conjunction with a monochromator. Because the typical super-bandgap absorption coefficients is typically orders of magnitude larger than the sub-bandgap coefficient, SPS is vulnerable to the spurious contribution of high-order diffraction peaks and stray light. Use of a monochromator where these effects are as small as possible is therefore highly recommended. If the measurement device is a static metal plate or an STM tip, the illumination also must be periodically chopped to allow for lock-in detection of the signal. Use of a chopper, however, must be avoided when using a Kelvin probe or an AFM tip, where lock-in detection is made possible by vibration of the probe itself. For some applications, use of an auxiliary light source (e.g. white light, laser light, UV light, etc.) allows for ‘photo-bias’ of the system and/or for additional quantitative analysis.2 Although this is beyond the scope of the present text, we have allowed for such an auxiliary source in the schematic set-up of Fig. 4.

The actual recording of an SPV spectrum is coordinated by a real-time computer program. This program controls the monochromator motor and thus wavelength changes, operates the control electronics of the probe, reads the measurement results by interfacing with the probe read-out electronics via an analogue-to-digital converter and finally stores the obtained spectrum for subsequent display and analysis. A typical spectrum takes only a few minutes to collect. The main limitation to the collection speed is due to surface states with long lifetimes. In extreme cases, such states may increase the spectrum collection time to several hours. For studies that focus on such states, chopping the illumination must be avoided and care must be taken to ensure that the measurement time is slow enough to achieve quasi-equilibrium at each wavelength. Conversely, if such states are not at the focus of study, their effect may be circumvented completely by using a chopping frequency higher than the inverse of the surface state lifetime. This is typically done in industrial applications of SPS, where the measurement time must be minimized for maximizing the throughput.

**APPLICATIONS OF SPS**

**Semiconductor bandgap and type**

The first elementary application of SPS that we discuss is the approximate determination of the semiconductor bandgap. This determination is based on the large increase in absorption coefficient near the bandgap energy $E_g$ found in most semiconductors. This increase brings about a significant change of the SPV signal, which is identified easily as a sharp change in slope of the SPV curve and often is the most significant one in a given spectrum. An example is shown in Fig. 5,33 where the slope changes related to the bandgaps of most known semiconductors have been analysed using this approach. In a particularly elegant application of this principle, Lagowski et al. have studied the SPV response of silicon-on-sapphire films.34 They have discovered that aside from the fundamental Si bandgap at ~1.1 eV, a second, distinct, knee in the SPV spectrum is found at ~1.4 eV. This value typically marks the onset of significant absorption at amorphous silicon films and therefore partial amorphization of the films was deduced.

The use of SPS for extraction of $E_g$ is, at heart, nothing more than an emulation of an absorption spectrum. However, as opposed to transmission spectroscopy, for example, SPS does not require light collection and therefore can be performed on arbitrarily thick samples (or on layers

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**Figure 4.** Schematic block diagram of a generic SPS set-up.
sandwiched within a heterostructure—see below) and does not require the sample to be removed from the substrate or grown on a transparent one.2 It is also inherently insensitive to reflection and scattering and thus is eminently useful for micro- and nanocrystallites.23

One must bear in mind that the obtained value of $E_g$ is only approximate. The nominal bandgap indeed is nearly always found within the onset of the largest SPV signal. However, this onset usually is relatively broad, the exact position of $E_g$ within it is by no means obvious and the error in $E_g$ is often $\sim 0.1$ eV and may be as large as 0.2 eV in some cases. This observation is true even for the clean surfaces of high-quality GaAs and InP single crystals shown in Fig. 5.

The broad onset of the super-bandgap SPV is due to the absorption of photons with an energy slightly below $E_g$, resulting from both the above-mentioned Franz–Keldysh effect and photo-assisted charge transfer between shallow states extending from the bandgap (also known as ‘tail states’) and one of the bands.34 Because SPS is inherently much more sensitive to sub-bandgap effects in the surface and SCR than absorption spectroscopy, ‘tail state’ effects become much more noticeable and an accurate value of $E_g$ can seldom be obtained from the SPS curve simply by inspection.

Detailed experimental comparisons between SPV and absorption spectra reveal that the two are often similar but never identical.35,36 It can be shown that a linear dependence of the SPV on the illumination intensity (achieved if the latter is low enough), an absorption length much larger than the diffusion length and an effective surface recombination velocity that is only weakly dependent on the illumination intensity, allow for the super-bandgap SPV spectrum to emulate properly the absorption spectrum.2 If these conditions are met, $E_g$ may be extrapolated quantitatively from the data, just as in transmission spectroscopy.37

We now turn our attention to determining the type (p or n) of semiconductor. This may be achieved with the help of the sign of the knee associated with the SPV onset: most semiconductor surfaces are depleted/inverted, which means that the bands of p-type semiconductors are bent downwards towards the surface, whereas the bands of n-type semiconductors are bent upwards. Because super-bandgap illumination typically tends to decrease the surface band-bending, this would result in a positive SPV in n-type semiconductors and a negative SPV in p-type semiconductors (Note: for CPD changes, the sign convention is opposite.) For example, the SPV spectra of n-type GaAs and p-type InP (shown in Fig. 5) clearly feature opposite onset signs that obey the above rules.

Although in many cases the type of semiconductor is known a priori, this is not always the case and SPS can become very useful in determining the semiconductor type. For example, SPS studies on free-standing porous Si films made from p-type Si revealed that the films may be of either conduction type, depending on the resistivity of the Si substrate used.39 In another example, SPS was used for fast and non-destructive verification of the semiconductor type in GaN films.40 This is very important because the p-doping of GaN is known to be non-trivial and subject to compensation by its native n-type doping.

If the band-bending is small, super-bandgap SPV mechanisms other than that of Fig. 1(b) may dominate. For example, etched CdSe quantum dot films were found to exhibit a p-type response in a humid ambient and an n-type response in a dry ambient, as shown in Fig. 6.41 Using photoelectron spectroscopy, however, these films were found to remain n-type at all times in terms of the position of the Fermi level. The ambient sensitivity of the ‘type conversion’ shown in Fig. 6, as well as other evidence, suggests that the SPV signal and the effective conductivity of these films are due primarily to preferential trapping of holes or electrons in a
Defect state characterization

A key strength of SPS is in determination of the energy position and type of surface states. Because photons of sufficient energy may excite charge carriers from a surface state to a band, or vice versa, we expect a knee in the SPV spectrum whenever the photon energy exceeds the threshold energy of a certain transition. If the latter involves excitation of electrons from the surface state to the conduction band [Fig. 1d(i)], a positive change in the surface charge is induced and hence a positive SPV (negative ∆CPD) is expected. Conversely, excitation of holes to the valence band [Fig. 1d(ii)] makes the surface charge more negative and a negative SPV (positive ∆CPD) is expected. Thus, the combination of the SPV threshold energy and slope sign makes the determination of the approximate position of the surface state within the bandgap possible.

As a first illustrative example, let us consider how SPS can be used to monitor metal-induced surface states,42–44 as shown in Fig. 5,53 after cleaving in UHV, neither the GaAs(110) nor the InP(110) surfaces display any knees associated with deep surface states, as expected for these surfaces. However, upon deposition of a very thin metallic overlayer, distinct sub-bandgap knees emerge. These knees, associated with a negative and positive CPD change at the Al/GaAs(110) and Au/InP(110) interfaces, respectively, indicate the formation of a surface state situated approximately ~0.8 eV below the conduction band edge and ~0.85 eV above the valence band edge, respectively. This study, as well as others cited above, provides clear-cut experimental evidence for the induction of gap states at metal/semiconductor interface by metal deposition.

Because SPS is contactless and non-destructive it can be applied not only to clean surfaces but also to real ones, in practically any ambient. This makes SPS highly suitable for a direct correlation of surface electronic structure with chemical treatments. One such area of active research is the study of passivation treatments.45–47 An illustrative example, in which the passivating effects of various liquids on the p-InP(100) surface was studied in situ, is shown in Fig. 7.48 The positive CPD change at ~1.3 eV found in all spectra shown is clearly due to the onset of band-to-band transitions in the InP sample, with its sign indicating a p-type sample, as appropriate. The SPV spectrum of the water-exposed sample (which is similar to that obtained in air; not shown) features two surface states: the positive CPD slope change at ~0.95 eV is due to a photoinduced population of a surface state situated ~0.95 eV above the valence band edge; and the negative CPD slope change at ~1.2 eV is due to a photoinduced depopulation of a surface state situated ~1.2 eV below the conduction band edge. Interestingly, exposure to HF eliminates the latter state but not the former. The opposite is true for exposure to H₂O₂.

Finally, exposure to an Na₂S solution results in removal of both surface states, in agreement with the known passivating action of this solution.

![Figure 7. Surface photovoltage spectra of the p-InP(100) surface in air and after successive immersion in (from top to bottom in lower energy part): A, 18 M H₂O₂; B, 0.4% HF; C, 30% H₂O₂; D, 1.3 M Na₂S solution. (After Ref. 48, reproduced by permission of the American Institute of Physics.)(Image 352x534 to 521x769)](https://example.com)

Other important areas of SPS applications include basic studies of surface electronic structure at well-defined clean surfaces,8,49 as well as studies of the impact of controlled gas adsorption in vacuum chamber processes.9,50,51,52 A representative example in which the p-Si(111) surface was investigated is shown in Fig. 8.53 A distinct difference

![Figure 8. Surface photovoltage spectra of the p-type Si(111) surface for different surface configurations. (After Ref. 53, reproduced by permission of the American Physical Society.)(Image 376x128 to 520x311)](https://example.com)
between surface state energies at the \((2 \times 1)\) and \((7 \times 7)\) surface configurations is apparent. Oxygen adsorption at the \((7 \times 7)\) surface greatly changes the SPV spectrum, such that positive SPV producing transitions to the conduction band are apparent.

Another promising SPS application of much recent interest is the characterization of organic semiconductors or organic treatments of semiconductors.\(^{35,36,46,47,54}\)

Although so far we have considered only surface states, SPS is sensitive to bulk states too. Accordingly, SPS has been used for studying Cr-related defects in GaAs,\(^{55}\) Fe-related defects in InP,\(^{56}\) and Mn-related defects in CdMnTe.\(^{57}\) The simplest distinction between surface and bulk states in SPS is obtained by examining whether the pertinent spectral feature disappears after a surface\(^{35,53}\) or a bulk (e.g. doping)\(^{35-57}\) treatment.

Additional quantitative analyses of the SPV spectra allow for a determination of densities, thermal and optical transition rates and spatial site of gap states. A detailed discussion is outside the scope of the present text (see Ref. 2), but we will say that such analyses usually are based on the SPV response to a systematic modification of one or more external parameters, e.g. time (for transient responses), illumination intensity, temperature, etc.

**Characterization of multilayer structures**

Beyond the study of surface and bulk properties, the application of SPS to heterostructures, multilayer structures and actual device structures has been most rewarding in recent years. The SPS of multilayer structures is illustrated by Fig. 9. This figure features the SPV spectra of a ZnO:Al/ZnO/Cds/Cu(In,Ga)Se\(_2\) layered structure used for the fabrication of thin-film solar cells.\(^{58}\) Distinct spectral ‘knees’ at \(\sim1, \sim2.4,\) and \(\sim3.1\) eV, corresponding to the bandgaps of Cu(In,Ga)Se\(_2\),CdS and ZnO, respectively, are clearly observed (the ‘feature’ at \(\sim1.5\) eV is an artefact due to a change of filter at that energy and should be ignored). The unequivocal identification of all three bandgaps confirms the above-mentioned theoretical prediction of SPS sensitivity to buried interfaces (see Fig. 2). The magnitude of the SPV signal is seen to increase with increasing annealing time (in air, at 200 °C) in agreement with the increase in overall solar cell efficiency with such annealing.

Spectral ‘knees’ are assigned to the various bandgaps in heterostructures just as in the simple SPS analysis discussed above. However, the interpretation of the slope sign of these ‘knees’ is considerably more complicated because in heterointerfaces the direction of the band-bending is not determined solely by depletion or accumulation and because some overlayers cause a reduction in SPV signal via simple absorption.\(^2\)

Some notable, recent applications of SPS to heterostructures include studies of defects, bandgaps and band-bending at Si/porous-Si bilayers,\(^{39,59}\) InP-based heterostructures,\(^{10,60}\) GaAs/AlGaAs heterostructures,\(^{61,62}\) the organic/inorganic \(p\)-dithioketopyrrolopurpyrrole (DTPP)/SnO\(_2\)/F heterojunction,\(^{35}\) \(\delta\)-doped GaAs layers,\(^{63}\) GaN/InGaN heterostructures\(^{60}\) and even BaTiO\(_3\)/Si heterostructures.\(^{64}\)

In a similar fashion, SPS allows for the characterization of quantum wells and other low-dimensional heterostructures.\(^{12,13,65,66}\) An illustrative example of the SPS of a multi-quantum-well (MQW) GaAs/AlGaAs structure is shown in Fig. 10.\(^{12}\) The spectral ‘knees’ at 1.38 and 1.78 eV correspond to the onset of band-to-band absorption in the GaAs epilayer (beginning at energies below the nominal bandgap due to the Franz–Keldysh effect) and the AlGaAs cap layer, respectively. In-between these two ‘knees’, the shape of the SPV spectrum resembles (an inverted) typical absorption spectra of MQW structures and the observed MQW-related minima agree well with calculated energy values of the 1HH–1E and 2HH–2E transitions. Note that before etching a non-negligible sub-bandgap SPV signal was apparent at photon energies <1.38 eV, indicating the presence of optically active gap states. Because no such signal was observed after etching, these states were located at the external AlGaAs surface and were not associated with the MQW region. Moreover, the SPV spectrum in the MQW

![Figure 9](image1.png)

**Figure 9.** Surface photovoltage spectra of ZnO:Al/ZnO/Cds/CIGS structures for various annealing times, in air, at 200 °C (After Ref. 58, reproduced by permission of the American Institute of Physics.)

![Figure 10](image2.png)

**Figure 10.** Surface photovoltage spectra of a GaAs/AlGaAs MQW sample before (solid line) and after (dashed line) etching. (After Ref. 12, reproduced by permission of the American Institute of Physics.)
absorption energy range has not changed at all (other than undergoing a uniform shift) after the etch, ascertaining that the signal SPV in the MQW absorption range is not interfered with by surface effects. Thus, all ‘symmetry-allowed’ heavy-hole–electron transitions have been resolved at room temperature.

Because SPV analyses of multilayer structures offer the possibility of performing contactless and non-destructive electrical and optical characterization of buried interfaces, they have found significant uses in the field of process monitoring and quality control of actual device structures. This is because the possibility of assessing the quality of a layered structure before any actual device processing takes place presents an opportunity for significant savings in time and money. Recent applications include the identification of defective batches and the prediction of ultimate performance of solar cells, the prediction of energy levels and lasing wavelength in modern laser heterostructures and the assessment of bandgap narrowing and ultimate gain of heterojunction bipolar transistors.

As an example of such studies, consider the recent characterization of an InGaAs/GaAs/AlGaAs vertical cavity surface-emitting laser, as shown in Fig. 11. It is readily observed that SPS resolves both the gain-providing 1C–1H transition and the lasing-wavelength-related ‘cavity mode’ , as well as a rich oscillatory structure above due to interference effects from the distributed Bragg reflector stacks. The measured SPV spectrum also is in very good agreement with the calculated dependence of the photoexcited carrier density on photon energy, also shown in Fig. 11. In fact, SPS is the first contactless technique to resolve all of these VCSEL features in one measurement, and it allows for a temperature-resolved determination of these quantities.

**CORRELATION WITH OTHER METHODS**

As with many other techniques, there is much to learn by combining SPS data with those of other experimental tools. The techniques that ‘naturally complement’ SPS broadly fall into two categories: other optical/electrical measurements and chemical analysis tools.

We begin by discussing the first category: the above-discussed, unique capability of SPS to identify the band with which charges communicate and therefore correctly position the surface state inside the bandgap has been used often to interpret unequivocally the results of photoluminescence or surface conductivity measurements. The latter techniques resolve the threshold energy of different transitions but not the band involved. Surface photovoltage spectroscopy also is used often to provide insight into the relation between surface or interface states and surface or interface electronic properties. For example, the Schottky barrier height in metal/semiconductor junctions is almost always found to agree, usually to better than 0.1 eV, with the position of the dominant surface states found by SPS, constituting a direct experimental verification of Bardeen’s model of Fermi-level pinning by surface states. In another example, SPS was used to establish a distinct correlation between surface states and the surface recombination velocity, measured independently using time-resolved photoluminescence (trPL). The more ‘rich’ with surface states the SPV spectrum was, and the closer the surface states were to midgap, the higher the (independently measured) surface recombination velocity was, in perfect agreement with defect-assisted recombination theory.

Similarly, other optoelectronic tools often assist in the unequivocal interpretation of SPS data. For example, one of the most popular methods of distinguishing between surface and bulk states is comparing SPV and photoconductivity spectra. The latter spectra are inherently insensitive to surface transitions because the photocurrent is collected from the entire bulk of the sample, so that the contribution of the SCR is typically negligible. Therefore (with some caveats in ‘pathological’ cases), transitions appearing in both types of spectra usually are attributed to bulk transitions, whereas transitions appearing in the SPV spectra alone are assigned to surface states. Another example is that independent surface recombination velocity measurements by trPL often are very useful in assessing the relative importance of the surface recombination velocity and the equilibrium surface band-bending in determining the magnitude of the SPV signal.

As a non-trivial example of the power inherent in a combination of several optoelectronic spectroscopies, we consider the comprehensive characterization of defects in thin GaN films by photoluminescence, SPV, photoconductivity and internal photoemission spectra, all four of which are shown in Fig. 12. The photoluminescence data, aside from the bandgap feature at ~3.4 eV, show a broad defect-related luminescence peak at ~1.6–2.5 eV, usually known as the ‘yellow luminescence’ peak. A distinct SPS signal is observed in the same defect-related spectral range and its intensity is in perfect correlation to that of the luminescence data. Using some quantitative arguments, this signal was attributed to surface states and thus the usual sign analysis of the SPS data allowed an unequivocal assignment of the related defect states to transitions involving the conduction band. However, a related, intensity-correlated signal also
is observed clearly in the bulk-sensitive photoconductivity data. This seeming contradiction led to the hypothesis of similar defects situated at internal grain surfaces and not just at the external free surface. The hypothesis was strongly supported by testing and confirming a key prediction of it—an exponential dependence of the photoconductivity signal on the SPV signal. Finally, the existence of the same transitions in internal photoemission spectra of metal-covered films indicated the existence of similar states at the metal/GaN interface as well. It showed further that these states pin the interface Fermi level but may be unpinned partially by sub-bandgap illumination (in this case causing the Schottky barrier to increase by almost 1 eV).

The second category of SPS-complementing tools consists, essentially, of any analysis that allows us to gain insight into the chemical origin of the gap-state changes observed in SPS. The most obvious example is the test of various known chemical treatments, as in Fig. 7 or Refs 44, 46 and 47, for example. However, an extensive chemical characterization of SPS data is afforded most easily by traditional surface science tools, notably photoelectron or Auger electron spectroscopies. The use of such tools in tandem with more traditional analytical tools, we have tried to demonstrate just how powerful SPS can be in a realm of semiconductor science that often has proved to be quite difficult: the cross-roads of physics, chemistry and electrical engineering.

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CONCLUDING REMARKS

In this review paper, we have attempted to show how SPS may provide a detailed picture of the electronic structure, in a manner that bridges the gap between the chemical, physical, optical and electrical properties of semiconductors. We have shown that SPS features a theory that is relatively straightforward (at least at the qualitative level) and typical experimental set-ups that make the method contactless, non-destructive, ambient insensitive and capable of any lateral resolution, in principle down to the atomic scale. By discussing selected examples of its use, both in itself and in tandem with more traditional analytical tools, we have tried to demonstrate just how powerful SPS can be in a realm of semiconductor science that often has proved to be quite difficult: the cross-roads of physics, chemistry and electrical engineering.