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Band gap determination of semiconductor powders via surface photovoltage spectroscopy

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Surface photovoltage spectroscopy (SPS) is introduced as a powerful tool for band gap determination of semiconductor powders. The main advantage of SPS is that scattering and reflection do not interfere with the spectra. Therefore, it does not suffer from the inherent limitations of transmission/reflection based spectroscopies, most notably diffuse reflectance spectroscopy (DRS). The principles of the approach are presented and its usefulness is demonstrated by comparing it with DRS for band gap determination of GaAs, InP, CdTe, CdSe, and CdS semiconductor powders. © 1999 American Institute of Physics. [S0021-8979(99)01222-0]

I. INTRODUCTION

One of the most important parameters which characterize a semiconductor is its band gap energy, E_g . In a nondegenerate bulk semiconductor, this parameter is easily determined by detecting the optical absorption threshold using, e.g., transmission (absorption) spectroscopy or modulated specular reflectance spectroscopies. However, these techniques are not applicable to semiconductor powders, due to the large scattering component.

The most developed optical tool applicable to the study of powders is diffuse reflectance spectroscopy (DRS).¹ Diffuse reflectance refers to radiation which is reflected in all directions, as opposed to specular reflectance which has a defined angle of reflection to the incident radiation. The former occurs in samples with particles oriented in different directions and the latter occurs at an optically smooth surface. The generally accepted theory of DRS was developed by Kubelka and Munk.² Based on the assumption that diffuse reflectance arises from absorption and scattering of light by a surface, these authors have developed a simple expression which translates the diffuse reflectance spectrum to the absorption spectrum.

DRS is widely used in industrial applications and in the study of solid–solid reactions, absorbed species, surface phenomenon, etc. However, it has several significant limitations. First, the Kubelka–Munk theory is valid only for weakly absorbing substances.^{1,3} Second, it is not valid in the presence of a specular reflectance component. Third, for crystallite sizes smaller than $\sim 10 \mu\text{m}$, DRS has been reported to systematically underestimate the band gap, with an error which increases with decreasing crystallite size.⁴ Fourth, DRS measurement of powders requires a relatively large amount of powder ($>0.1 \text{ g}$). Finally, there are no universal standards for quantitative DRS analysis and most of the standards that are in use (MgO , BaSO_4 , and MgCO_3) must be

continually renewed because their surface deteriorates with time.

In this article, we show that surface photovoltage spectroscopy (SPS) is eminently suitable for band gap determination of semiconducting powders. First, we discuss the principles of operation of SPS and show that it is *inherently* immune to the above mentioned shortcomings of DRS. We then demonstrate the strength of SPS by comparing between SPS and DRS results obtained from different semiconductor powders.

II. PRINCIPLES OF BAND GAP DETERMINATION VIA SPS

SPS measurements are based on monitoring illumination-induced changes in the surface potential, as a function of incident photon energy.^{5–7} In principle, a surface photovoltage (SPV) arises from the photoexcitation of excess free carriers, which is followed by their redistribution in the sample. This redistribution changes the potential distribution in the sample (to which it is interrelated via the Poisson equation) and in particular changes the surface potential. Changes in the latter can be measured in a contactless, non-destructive manner by several capacitance-coupling based methods, discussed in detail in Ref. 7.

The dominant physical mechanisms by which super-band gap illumination results in SPV generation are shown in Fig. 1.⁷ In the first mechanism [Fig. 1(a)], the electric field present in the surface space charge region (SCR) causes the electron and hole to drift in opposite directions. This creates a macroscopic electrical dipole, which produces an electric field in an opposite direction to the original one and reduces the surface potential barrier. In the second mechanism [Fig. 1(b)], either electrons or holes are preferentially trapped at surface defects. This effectively charges the surface and thus modifies the surface potential. Typically, the first mechanism is the dominant one in bulk samples. The second one is usually apparent in bulk samples only if the surface potential barrier is fairly small, but increases in importance with de-

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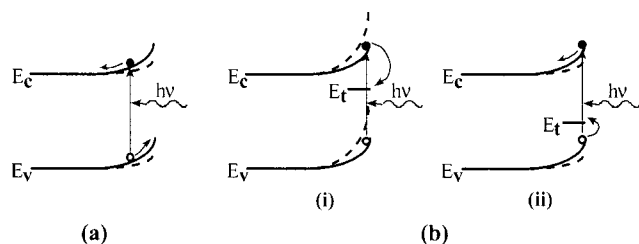


FIG. 1. Schematic band diagram of a semiconductor surface, illustrating mechanisms for SPV generation by super-band gap illumination: (a) carrier separation under an electric field. (b) Preferential carrier trapping - (i) electron trapping, (ii) hole trapping. E_c and E_v denote the conduction band minimum and valence band maximum, respectively. E_t -trap level. Solid and dashed lines indicate band positions in the dark and under illumination, respectively. Straight arrows denote carrier generation, curved arrows denote carrier trapping.

creasing crystallite size, because of an increasing surface to volume ratio.⁷ Accordingly, it has recently been shown to dominate the SPV observed in CdSe nanocrystallite films.⁸

Based on the above considerations, it is apparent that a significant SPV signal is expected to arise at photon energies exceeding the semiconductor band gap. Therefore, the band gap value of bulk semiconductors has frequently been estimated simply by detecting the onset of the super-band gap SPV signal, either by pinpointing the corresponding knee in the SPV spectrum^{9,10} or by looking for the maximum of its derivative.^{5,11} Such analyses usually yield a band gap value which underestimates the real band gap by several tens of meV, but seldom by more than 100 meV.⁷

The discrepancy between the real and measured band gap value is due to SPV generation by subband gap illumination, which blurs the true onset of the super-band gap SPV signal. Two mechanisms for subband gap SPV are shown schematically in Fig. 2. The most common one [Fig. 2(a)] involves the direct modification of the surface charge, and hence potential, by excitation of trapped carriers. The second involves the formation of electron hole pairs via photon-assisted tunneling (also known as the Franz-Keldysh effect).¹²

It has been shown that in cases where (a) the injection level of excess carriers is low, (b) the absorption length is much larger than the diffusion length, and (c) the surface recombination velocity is independent of the injection level,

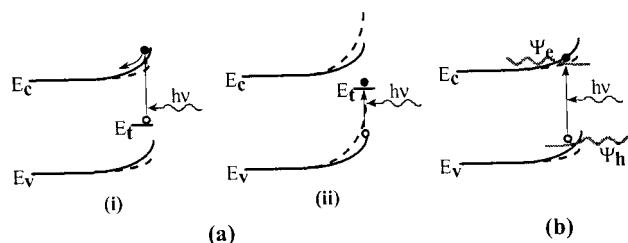


FIG. 2. Schematic band diagram of a semiconductor surface, illustrating mechanisms for SPV generation of subband gap illumination: (a) excitation of trapped carriers: (i) electron excitation, (ii) hole excitation. (b) Franz-Keldysh absorption - ψ_e and ψ_h denote electron and hole wave functions, respectively. Solid and dashed lines indicate band positions in the dark and under illumination, respectively. Straight arrows denote carrier generation, curved arrows denote carrier trapping.

the dependence of the SPV on the photon energy mimics that of the absorption spectrum.⁷ The latter is well known to exhibit a $\alpha^n \sim h\nu - E_g$ behavior, where α is the absorption coefficient, $h\nu$ is the photon energy, and n is 2 or 1/2 for direct or indirect semiconductors, respectively. An extrapolation of $(SPV)^2$ or $(SPV)^{1/2}$ vs $h\nu$ plots was therefore used to obtain highly accurate (~ 10 meV) values of the band gap in various semiconductors.^{13,14}

The above-discussed principles of SPS-based band gap determination for *bulk* semiconductor samples are immediately applicable to semiconductor *powders* as well, with no intrinsic loss of accuracy. This is because all that is required is super-band gap photon absorption, followed by *any* charge separation mechanism. This immediately overcomes a major disadvantage of DRS, namely, that its accuracy is limited for grain sizes smaller than 10 μm . SPS also overcomes the other disadvantages of DRS, mentioned in the introduction. Because a sizable SPS signal is frequently obtained from films that are as thin as several tens of nm,¹⁵ it is reasonable that in many cases the measurement will succeed for as little as 1 ML of crystallites (or even less, depending on crystallite size). By definition, SPS only senses light that is absorbed. Therefore, the nature and degree of scattering and/or reflection processes and the relative strength of absorption are inherently of no consequence. Moreover, no reflection standard is necessary as no reflection is measured. On the disadvantage side, the sensitivity of SPS decreases with decreasing semiconductor band gap and increasing temperature.^{5,7} Therefore, studies of small-band gap materials may necessitate sample cooling.

III. EXPERIMENT

III-V semiconductor samples of GaAs (AXT, Si doped to $n \sim 10^{17} \text{ cm}^{-3}$) and InP (Crystacomm, Zn doped to $p \sim 4 \times 10^{16} \text{ cm}^{-3}$), as well as II-VI semiconductor powders of CdSe (Aldrich, 99.99% purity), CdTe (CERAC Specialty Inorganics, 99.999% purity), and CdS (Aldrich, 99.995% purity) were obtained commercially. Both crystals and powders were mechanically ground until a fine powder with a typical crystallite size smaller than 1 μm (as verified by scanning electron microscopy) was obtained. Quantum CdS particles were prepared by heating a dimethylsulfoxide solution containing 2.8 mM of cadmium acetate and 2.5 mM of elemental sulfur at 120 $^\circ\text{C}$ for 15 min. Their typical crystallite size was ~ 4 nm.¹⁶

All samples were prepared by spreading a thin layer of a conduction carbon paint (20% solids colloidal graphite in isopropanol, SPI supplies) on a 10 Ω/\square SnO_2 :F-coated glass (NESA glass, Nippon Sheet Glass Co.). This was followed immediately by sprinkling the semiconductor powder over the wet surface. After the paint was completely dry, excess powder was removed. Typically, ~ 1 ML of crystallites was deposited.

The surface photovoltage (SPV) has been monitored in air at room temperature using a commercial Kelvin probe unit (Besocke Delta Phi) with a sensitivity of ~ 1 mV. For spectroscopy purposes, the sample was illuminated by a 600 W tungsten-halogen lamp passing through a 0.5 m grating

monochromator (Jobin-Yvon 270M). The output of the monochromator is wavelength dependent and is typically in the μW range.

DRS measurements were carried out in air at room temperature in a spectrophotometer equipped with an integrating sphere (Jasco V-570). Spectra were recorded with a scanning speed of 100 nm/min. A MgCO_3 sample was used as a reference. The spectra are given as plots of the Kubelka–Munk correction function,^{1,2} automatically converted from the raw diffuse reflectance data by the spectrophotometer software.

IV. RESULTS AND DISCUSSION

The results of both SPS and DRS for three representative semiconducting powders are shown in Fig. 3. In the SPS data, extrapolation of the $(\text{SPV})^2$ versus photon energy curves, as explained above, was employed for precise band gap determination. Band gap values of 1.33, 1.41, and 1.68 eV, were found for the InP, GaAs, and CdSe samples, respectively. These values are in excellent agreement (~ 20 meV at most) with the commonly accepted values of 1.34, 1.43, and 1.7 eV, respectively. At the same time, the Kubelka–Munk corrected DRS data are systematically biased in the direction of a smaller band gap. Moreover, they usually do not feature transition edges which are as sharp as those of the SPV spectra, further limiting the accuracy of the measurement.

In some powders, a significant contribution of subband gap absorption in surface states was apparent. Two examples of such behavior are shown in Fig. 4. In both cases, the SPV at super-band gap photon energies still possessed a significant subband gap contribution, so that the extrapolation procedure applied in Fig. 3 could not be used. This is especially apparent in the CdTe sample [Fig. 4(b)], where the subband gap response is actually larger than the super-band gap one (and of opposite polarity, so that it dominates the spectrum). We therefore resorted to a simple determination of the band gap energy via identification of the band gap related knee energy. This results in values of 1.39 and 1.47 eV for the GaAs and CdTe samples, respectively. These values are within ~ 40 and ~ 30 meV, respectively, of the nominal band gaps—still a very high accuracy, and still better than that afforded by DRS of the same samples, also shown in Fig. 4.

Two comments regarding the contribution of surface states are in order. First, in many cases, the surface state response is much slower than that of the bulk. It can therefore be quenched by using light chopped at a sufficiently high frequency,¹⁷ resulting in further improvement of the accuracy. Second, the surface state contribution can also be used advantageously for, e.g., assessing the success of surface-passivation treatments of crystallites.

SPS is easily applicable even to powders with very small crystallite sizes. This is illustrated in Fig. 5, which features SPV spectra of two CdS powders, one with a $\sim 1 \mu\text{m}$ crystallite size, the other with a ~ 4 nm crystallite size. It is well known that if the crystallite size is small enough, its effective optical band gap will increase due to the quantum size effect.¹⁸ Indeed, it is readily apparent that the sample with smaller crystallites displays a significant blueshift with re-

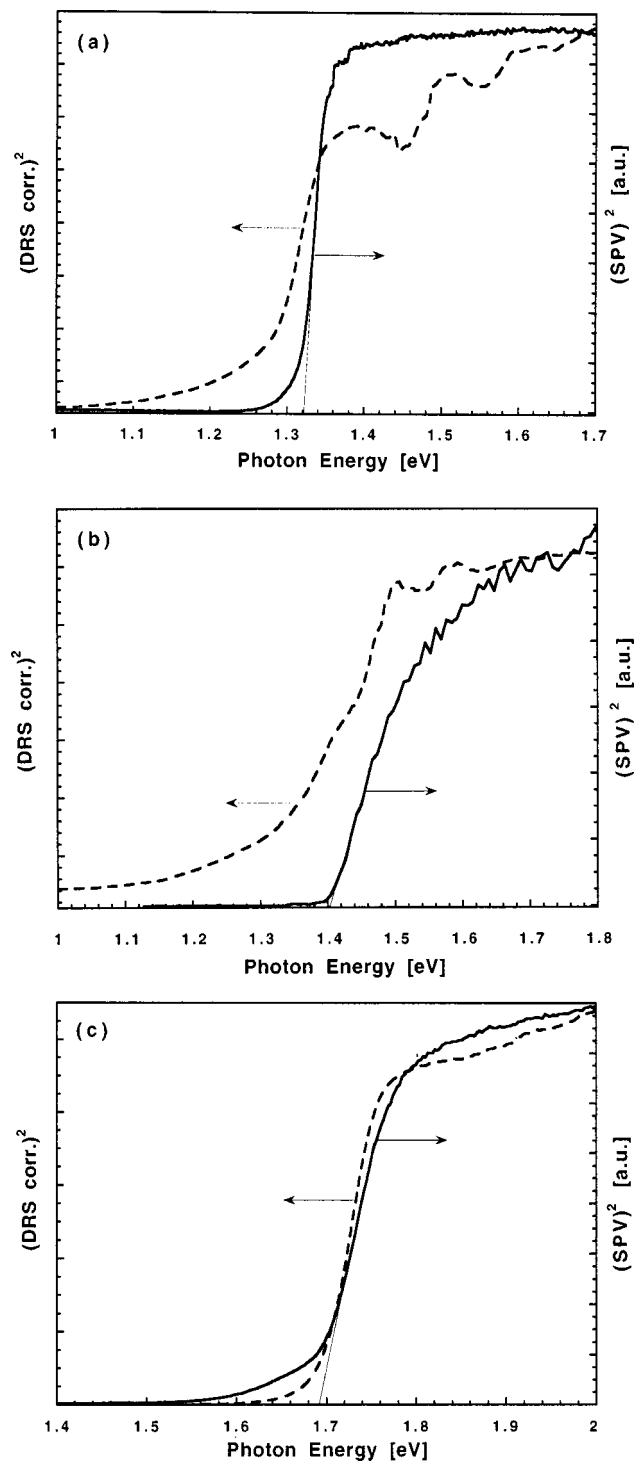


FIG. 3. SPS (solid lines) and DRS (dashed lines) data of semiconductor powders *not* displaying a significant subband gap absorption: (a) InP, (b) GaAs, (c) CdSe. The corrected DRS have been squared to allow a fairer comparison with the surface photovoltage spectra.

spect to the sample with larger crystallites. Unfortunately, a precise determination of band gap values was not possible here, due to significant changes in the photon flux at the relevant spectral region. Nevertheless, if we assume that the relative shift between the two SPS curves is a rough indicator of the band gap shift, then its value of ~ 0.25 eV is well within the theoretically expected blueshift for CdS crystallites of this size.¹⁹

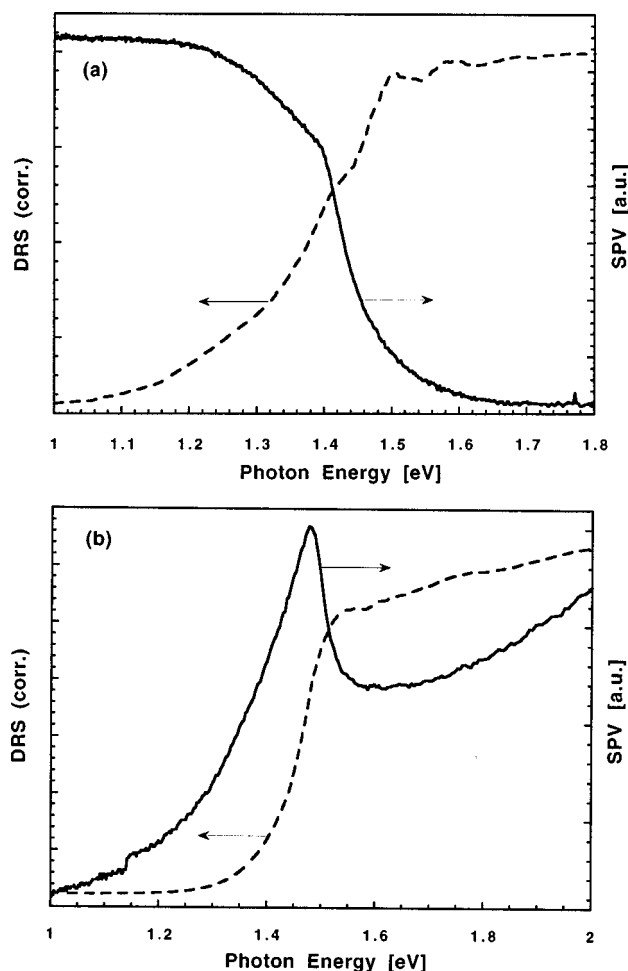


FIG. 4. SPS (solid lines) and DRS (dashed lines) data of semiconductor powders displaying a significant subband gap absorption: (a) GaAs, (b) CdTe.

We have also found SPS to be superior to DRS with respect to the minimum sample lateral dimensions allowed. In the samples studied, a typical minimum size of $\sim 2 \text{ cm}^2$ was required for obtaining a meaningful signal from DRS measurements. In SPS, we found a minimum size of ~ 0.1

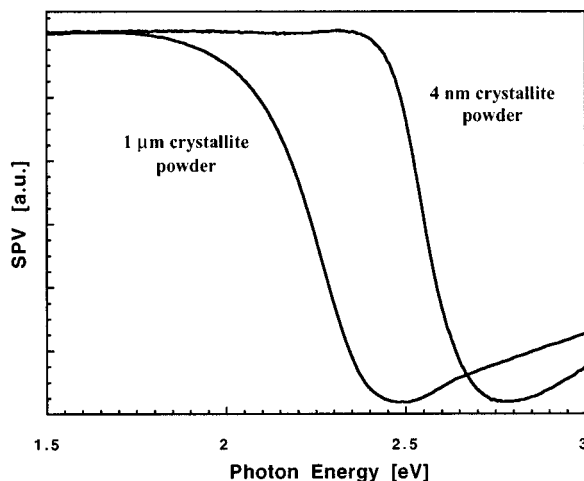


FIG. 5. SPS data of two CdS semiconductor powders with a $\sim 1 \mu\text{m}$ and a $\sim 4 \text{ nm}$ crystallite size.

cm^2 , which was limited only by the size of the Kelvin probe head. As sub- μm lateral resolution is afforded by many advanced Kelvin probes,⁷ one could potentially extract the band gap even from several crystallites of powder, given the right equipment.

Physically, all advantages of SPS stem from the fact that absorption spectra are emulated via voltage spectra, while reflection and transmission are inherently ignored (they may reduce the sensitivity of the measurement but will not interfere to any major effect with the spectral shape of the samples). In principle, any technique which can similarly emulate the absorption via another quantity should work equally well. This is apparently true for photothermal spectroscopies.²⁰ A unique feature of SPS, however, is that it provides significant hints to the dominating transport mechanism (see Fig. 1). Specifically, the photovoltaic sign indicates the effective conductivity type of the layer.⁷ We caution that one should beware of simplistic sign assignments. For example, if the dominating transport mechanism is separated by a SCR [Fig. 1(a)], the photovoltaic sign may change according to the relative importance of the front (crystallite/air) and back (crystallite/substrate) SCRs.^{7,15} Nevertheless, substantial physical conclusions can be obtained from carefully designed experiments to elucidate the transport mechanism (see, e.g., Ref. 8).

V. CONCLUSIONS

In this article, we have shown that SPS can be used successfully for determining the band gap energy of semiconductor powders, by using it to extract band gap values of several notable III–V and II–VI semiconductors. We have shown that because surface photovoltage spectral shapes are not affected substantially by scattering and reflection, SPS does not suffer from the inherent limitations of DRS. Therefore, it is successfully applied to powders of very small crystallite size and/or quantity, where DRS often fails. We have further shown that accuracies better than $\sim 10 \text{ meV}$ can be achieved in the absence of a significant surface state contribution to absorption. Even in the presence of such a contribution, an accuracy better than 100 meV is regularly obtained.

ACKNOWLEDGMENT

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