Journal of Electron Spectroscopy and Related Phenomena 185 (2012) 152–158

Contents lists available at SciVerse ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Utility and constraint on the use of pump-probe photoelectron spectroscopy for detecting time-resolved surface photovoltage

Shin-ichiro Tanaka*

The Institute of the Industrial and Scientific Research, Osaka University, 567-0047 Mihogaoka, Ibaraki, Osaka, Japan

ARTICLE INFO

Article history:
Received 23 January 2012
Received in revised form 8 June 2012
Accepted 8 June 2012
Available online 16 June 2012

Keywords:
Surface photovoltage
Time-resolved two-photon photoelectron spectroscopy
Semiconductor surface

ABSTRACT

Utility and constraints on using the pump-probe photoelectron spectroscopy for detecting the time-resolved surface photovoltage on the semiconductor surface are discussed by solving the equation of motion for the electron from the sample to the analyzer. The escape time, which is defined as the time for the electron to achieve the 99% of the photovoltage, determines the basic temporal resolution. It can be derived from a simple formula with the pump beam radius and the initial kinetic energy of the electron and lies in a range of nano seconds with a usual experimental condition so far. However, an analysis revealed that a time constant for the decay in the SPV can be correctly measured with the decay in the kinetic-energy shift as a function of the pump-probe time difference even for a much shorter time constant than the escape time. Meanwhile, the value of the kinetic-energy shift does not agree with the true SPV. The relation between the true SPV and the observed kinetic-energy shift is estimated.

1. Introduction

Surface photovoltage (SPV), which is the phenomenon that the electronic field is provided by the illumination of light at the semiconductor surface, is one of the key issues which govern the efficiency of the photoelectric devices and has been extensively studied theoretically and experimentally for many years [1,2]. Recently, the time-resolved measurement of SPV, particularly by using a time-resolved photoelectron spectroscopy (PES) of a pump-probe type, attracts attention since it promises to reveal the carrier dynamics in the semiconductor [3–13]. In this method, the laser pulse of a few electron volts is used as a pump beam to produce the SPV, and the time-delayed photons from the synchrotron radiation source [3–9] or the higher harmonics of the laser pulse [10–13] is used as a probe pulse to detect the SPV. Reflecting the development of the laser technique and synchrotron radiation, this method will probably be more popular and appealing for many researchers.

The time resolution of the optical pump-probe method is usually limited by the temporal widths of the pump and probe photon pulses. Thus, if the pulse laser of, say, 100 fs (it is rather easily achieved with a TiS-based mode-locked laser system these days) is used, it is conceivable that the temporal resolution of this range could be achieved. However, this idea seems questionable in the case of the detection of temporal change in SPV by the pump-probe PES, because the change in the electron energy is achieved by the acceleration/deceleration during the travel from the sample to the analyzer and the memory of the potential on the surface at the ejection time may be lost during the travel. If the electron with a kinetic energy of, for instance, 10 eV emits from the sample surface toward the entrance of the electron spectrometer that is separated by 5 cm from the sample, it takes about 27 ns. This is much longer than the pulse width of the femtosecond pulse laser and the temporal resolution might be limited by the travelling time of the electron in the worst case.

This problem in the detection of SPV by the pump-probe PES has been discussed by some researchers [7,9]. W. Widdra et al. cautioned that the onset in their time-resolved SPV measurement at the negative time-delay does not reflect the true temporal evolution of the SPV [7]. D. Lim and R. Height stated that the temporal evolution of the SPV can be accurately investigated as far as its timescale is longer than “escape time”, which will be discussed more detail in this paper. It was 2.5 ns in their experimental condition (note that they used a much shorter pulse, that is the higher harmonics of the 35-femtosecond pulse as a probe) [9]. On the other hand, much shorter lifetimes (in a range of ps) were experimentally observed in the energy shift in PES as a function of the pump-probe time difference (Δt) [6,10–12]. To resolve this paradoxical situation, a systematic analysis which allows us to estimate the utility and constraint of the pump-probe PES when applying it to the detection of the temporal evolution of the SPV is highly desired. In this paper, I present a quantitative guideline for using the pump-probe PES on the time-resolved SPV measurement by systematically resolving the classical equations of motion of the electron. This will help researchers who are interested in

---

* Tel.: +81 6 6879 8491; fax: +81 6 6879 8494.
E-mail address: stanaka@sanken.osaka-u.ac.jp

0368-2048/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elspec.2012.06.003

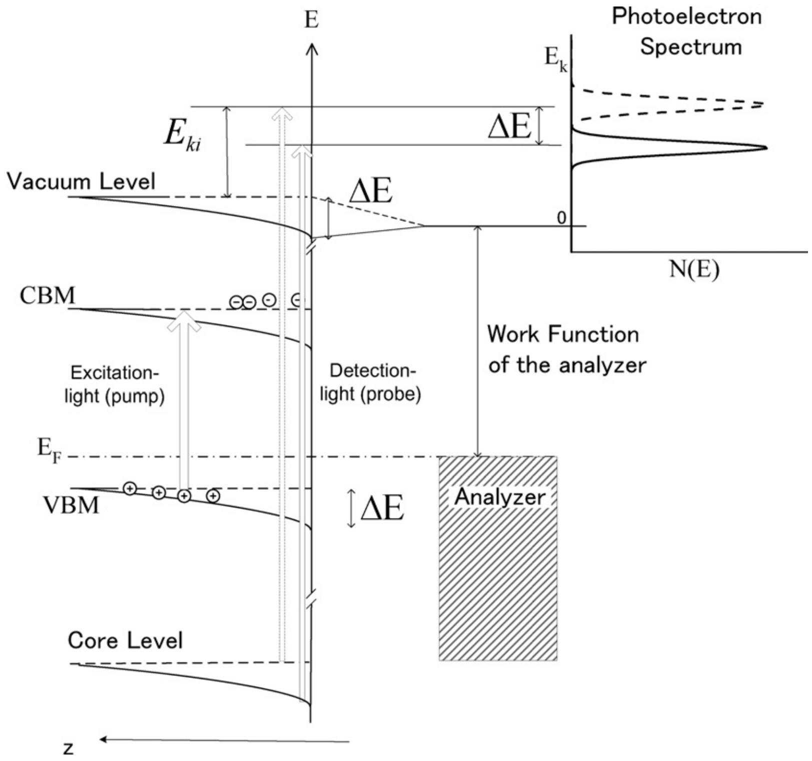

Fig. 1. Schematic drawing of the diagram for the surface photovoltage and its detection by the photoelectron spectroscopy. The solid lines show the energies of the relevant states, which are the vacuum level, the conduction band minimum (CBM), the valence band maximum (VBM), the core level, and the surface states, of the semiconductor without an excitation light. When the excitation (pump) light illuminates the semiconductor, the additional carrier is produced, and the energies of these states are shifted in energy ΔE as shown by dotted lines. The energy of the electron ejected from (for example) the core level by the photoexcitation with the detection (probe) light is analyzed by the electron spectrometer after the acceleration or deceleration by the electronic field. When the sample is illuminated by the excitation-light (dotted lines), the kinetic energy (E_k) obtained with the electron spectrometer is shifted in energy than that without the photoexcitation (solid lines) in the photoelectron spectroscopy. The initial kinetic energy of the electron at the ejection (E_{ki}) is indicated for the case that the sample is photo-excited.

measuring the time-resolved photoelectron spectroscopy with a newly developed pulsed light source such as the free electron laser.

2. The electron energy shift due to the static SPV

Fig. 1 shows a simple schematic drawing for the picture of the SPV formation and detection. When the light creates the additional carriers both at the valence and conduction bands of the semiconductor, these carriers move due to the electronic field in the space-charge region of the semiconductor and these separated positive and negative carriers (partly) compensates the band bending by the provided potential which is indicated as ΔE in Fig. 1. This is the so-called SPV. The photoelectron spectroscopy, which is commonly used for the investigation of the electronic state of the semiconductor and its surface, can be used for monitoring the SPV as discussed below. Since the escape depth of the photoelectron is usually much shorter than the length of the space-charge-region, the energy of the ejected electrons is only determined by the potential near the surface. It is usually assumed that the band structure is not significantly changed by the light illumination, thus the electron binding energy with referred to the valence band maximum (VBM) is assumed to be unchanged. The initial kinetic energy of the electron E_{ki} is defined as the difference between the vacuum level and the electron energy of the photoexcited state and does not change by the illumination. However, the position of the vacuum level changes with respect to the Fermi energy (E_F) by the added SPV (ΔE). Therefore, the photoelectron spectrum is shifted in kinetic energy by ΔE without changes in the peak shape. Let me describe it from the viewpoint of flying electrons from the sample to the electron analyzer. Without the illumination, since the equilibrium in energy between the sample and the analyzer is achieved with respect to the E_F, the sample surface can be considered biased by the difference in the work functions between the sample and the electron analyzer. The electrons are thus accelerated (or decelerated) accordingly during the flight from the sample to the entrance of the analyzer, and changed in the kinetic energy according to the bias voltage. When the new potential change ΔE is added at the light-spot area on the sample due to the SPV, the acceleration/deceleration energy is additionally changed by ΔE, and thus the kinetic energy of the electrons is changed by ΔE, enabling the measurement of the SPV.

According to this picture, the most important matter for measuring the temporal evolutions of the SPV with the PES seems the time when the acceleration (or deceleration) is completed. If the SPV changes earlier before completing the acceleration, it is not expected to monitor the SPV accurately. This was referred to as “escape time” by D. Lim and R. Height [9]. They considered it as a temporal resolution of the method, since the accuracy in the temporal evolution longer than this time is guaranteed. The first aim of this paper is a quantitative estimation of this quantity by evaluating the potential near the surface.

First, the two-dimensional SPV distribution on the sample surface is analyzed. The photon intensity as a function of the distance r from the spot center is $I(r) = I_0 \exp\left(-2r^2/R_0^2\right)$ where the Gaussian profile is assumed, I_0 is the intensity at the spot center, and R_0 is the spot radius. According to the previous studies [8,14], the SPV ΔE is approximately shown as $\Delta E = \alpha k_B T \ln[1+\gamma I]$, where I denotes the photon intensity, α and γ denotes the parameters that can vary with the sample and wavelength of the photon. Therefore, SPV on the sample surface (i.e., $z = 0$) as a function of the distance r from the spot center can be written as $\Delta E(r) = \Delta E_c/\ln(1+\eta)\ln\left[1+\eta\exp\left(-2r^2/R_0^2\right)\right]$, where ΔE_c denotes $\alpha k_B T \ln[1+\gamma I_0]$