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Dynamics and control of recombination process at semiconductor surfaces, interfaces and nano-structures

Hideki Hasegawa [a,*], Taketomo Sato [a], Seiya Kasai [a],
Boguslawa Adamowicz [b], Tamotsu Hashizume [a]

[a] *Research Center for Integrated Quantum Electronics (RCIQE), Graduate School of Information Science and Technology, Hokkaido University, N13, W8, Sapporo 060-8628, Japan*
[b] *Department of Applied Physics, Silesian University of Technology, Krzywoustego 2, 44-100 Gliwice, Poland*

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Abstract

Characterization methods and fundamental aspects of surface/interface states and recombination process in Si and III–V materials are reviewed. Various measurement considerations are pointed out for the conventional metal–insulator–semiconductor (MIS) capacitance–voltage (*C*–*V*) method, a contactless *C*–*V* method, and the microscopic scanning tunneling spectroscopy (STS) method, and general features of surface states are discussed. Surface states are shown to have U-shaped distributions of donor–acceptor continuum with a characteristic charge neutrality level, E_{HO}. Rigorous simulation of dynamics of surface recombination process has shown that the effective surface recombination velocity, S_{eff}, is not a constant of the surface, but its value changes by many orders of magnitude with the incident light intensity and the polarity and amount of fixed charge. From this, new methods of surface state characterization based on photoluminescence and cathodoluminescence are derived. Attempts to control surface states and Fermi level pinning at metal semiconductor interface and free surfaces of nano-structures are presented as efforts toward "nano-photovoltaics".

Keywords: Surface states; Surface recombination; Fermi level pinning; Capacitance voltage method; Tunneling spectroscopy; Nano-structures

1. Introduction

Rapid progress continues in the research of solar cells for a viable, clean and renewable energy source. Trends are toward use of new materials, toward use of thinner films and new structures, and even toward exploitation of nano-structures (Corkish et al., 2002). It is well known that surface recombination through surface/interface states is a major loss mechanism for photo-generated carriers. Obviously, its importance increases as the geometrical feature sizes of the solar cell structures are reduced.

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[*] Corresponding author. Tel.: +81 11 706 7170; fax: +81 11 757 1165.
E-mail address: hasegawa@rciqe.hokudai.ac.jp (H. Hasegawa).

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Nomenclature

N_{ss}	surface state density ($cm^{-2}\,eV^{-1}$)	U_s	surface recombination rate ($cm^{-2}\,s^{-1}$)
E_{oj}	surface state distribution parameter (eV)	σ	capture cross-section of the surface state (cm^2)
E_{HO}	sp^3 hybrid orbital energy (eV)	n	density of electron (cm^{-3})
E_c	conduction band minimum (eV)	p	density of hole (cm^{-3})
E_v	valence and maximum (eV)	ϕ	photon flux intensity ($cm^{-2}\,s^{-1}$)
E_g	energy band gap (eV)	α	adsorption coefficient (cm^{-1})
S	surface recombination velocity ($cm\,s^{-1}$)	ϕ_B	Schottky barrier height (eV)
S_{eff}	effective surface recombination velocity ($cm\,s^{-1}$)	χ	electron affinity (eV)
v_{th}	thermal velocity of carrier ($cm\,s^{-1}$)		

The purpose of this paper is to review a series of work done by authors' group on the fundamental aspects of surface/interface states and recombination process, including their characterization methods as well as the method to control the surface recombination process and Fermi level pinning. Although the data is mostly presented on Si and III–V materials, underlying physics, analysis methods and control technologies seem to be applicable to other new materials and new structures.

We start from the electrical characterization methods of the properties of surface/interface states lying at the passivated semiconductor surfaces. In addition to the conventional metal–insulator–semiconductor (MIS) capacitance–voltage (C–V) method, a contactless C–V method (Takahashi et al., 1999), and the microscopic scanning tunneling spectroscopy (STS) method (Hasegawa et al., 2000) are discussed. Various measurement considerations are pointed out.

Then, general features of energy distribution of surface state density (N_{SS}) are discussed. It is shown that surface states have U-shaped distributions with a characteristic charge neutrality level E_{HO} in accordance with the disorder induced gap state (DIGS) model for Fermi level pinning (Hasegawa and Ohno, 1986). Subsequently, dynamics of surface recombination process is discussed, using a rigorous computer simulation program (Adamowicz and Hasegawa, 1998). It is shown that the effective surface recombination velocity, S_{eff}, is not a constant of the surface with a given N_{SS} distribution as usually assumed. Its value changes by many orders of magnitude with the incident light intensity and the polarity and amount of fixed charge. This analysis has led to two novel contactless analysis methods for unknown N_{SS} distributions, i.e., the photoluminescence surface state spectroscopy (PLS^3) method (Adamowicz et al., 2002) and the cathodoluminescence in-depth spectroscopy (CLIS) method (Ishikawa and Hasegawa, 2002a,b).

Finally, efforts toward "nano-photovoltaics" at authors' group are briefly presented. It is shown that Fermi level pinning at metal–semiconductor interfaces is greatly reduced at electrochemically prepared nanometer-sized contacts (Hasegawa and Sato, 2005), opening up hopes for forming electron-collecting and hole-collecting nano-contacts for semiconductor nano-structures without p–n junction. It is shown that the Si interface control layer (ICL)-based passivation is effective to arrays of MBE-grown quantum wires (QWRs) (Shiozaki et al., 2005). These efforts may lead toward the realization of new high efficiency solar cells based on QWR arrays to be utilized as power supply for intelligent quantum (IQ) chips (Hasegawa et al., 2004) for coming ubiquitous network society as well as in conventional photovoltaic applications.

2. Characterization methods of surface/interface states

2.1. Conventional capacitance–voltage (C–V) method for macroscopic characterization

Surface passivation by a suitable dielectric film is an important step for fabrication of solar cells, since minimization of surface recombination is a critical issue for maximization of the conversion efficiency. The most frequently used method to evaluate energy distributions of surface states (interface states) lying at passivated semiconductor surfaces is to construct metal–insulator–semiconductor (MIS) capacitors and carry out either high frequency or quasi-static