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Quantum confinement in semiconductor nanofilms: Optical spectra and multiple exciton generation

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Abstract

We report optical absorption and photoluminescence (PL) spectra of Si and SnO_2 nanocrystalline films in the UV–vis–NIR range, featuring discrete bands resulting from transverse quantum confinement, observed in the optical spectra of nanofilms for the first time ever. The film thickness ranged from 3.9 to 12.2 nm, depending on the material. The results are interpreted within the particle-in-a-box model, with infinite walls. The calculated values of the effective electron mass are independent on the film thickness and equal to $0.17m_o$ (Si) and $0.21m_o$ (SnO_2), with m_o the mass of the free electron. The second calculated model parameter, the quantum number n of the HOMO (valence band), was also thickness-independent: 8.00 (Si) and 7.00 (SnO_2). The transitions observed in absorption all start at the level n and correspond to $\Delta n = 1, 2, 3, \ldots$. The photoluminescence bands exhibit large Stokes shifts, shifting to higher energies with increased excitation energy. In effect, nanolayers of Si, an indirect-gap semiconductor, behave as a direct-gap semiconductor, as regards the transverse-quantized level system. A prototype Si–SnO_2 nanofilm photovoltaic cell demonstrated photoelectron quantum yields achieving 2.5, showing clear evidence of multiple exciton generation, for the first time ever in a working nanofilm device.

Keywords: Thin films; Quantum wells; Electronic structure; Optical absorption; Photoluminescence

1. Introduction

Lately, a lot of interest was created around quantum confinement (QC) effects in different materials, with numerous publications in this area; see for example [1]. Three-dimensional, two-dimensional and one-dimensional QC has been observed in quantum dots, quantum rods, and quantum films (quantum wells), respectively [1,2]. An excellent review on quantum well structures in thin metal films discusses transverse quantum confinement in metal nanofilms with a known number of atomic monolayers deposited on single-crystal substrates, and studied foremost by angle-resolved photoemission [3]. The measurements were predominantly performed for electrons with binding energies not exceeding 2–3 eV, and phase accumulation model was used to describe the wavefunction reflections from the substrate-film and vacuum-film interfaces and calculate the energies of the quantum well states [3]. Photoluminescence (PL) from a single 1.1 and 1.6 nm Si

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quantum well between two SiO_2 layers, in a very well-defined system formed starting from bulk crystalline Si, was partly attributed to quantum confinement in the transverse direction, namely the PL component with the energy dependent on film thickness [4]. As an example, 1.30 nm thick SiO_2–Si–SiO_2 QW structure exhibited 1.7 eV energy of the quantum-confined PL component [4].

Recently we published a series of papers devoted to exchange anticrossing resonance in sandwich structures employing nanocrystalline metal and semiconductor films in variable external magnetic fields, see for example [5,6]. The model we used in interpreting these spectra requires the existence of discrete electronic states in such films, as opposed to continuous zones present in bulk materials, which we assumed were generated by transverse quantum confinement (TQC) in all of the materials involved, including Si, SnO_2, Au, Pt, Fe, Co, Ni, Cr, Mn, and Eu nanofilms. Presently we report direct evidence for TQC in Si and SnO_2 nanofilms, in the form of their UV–vis–NIR optical absorption and emission spectra, for the first time. We also report for the first time that nanolayers of Si behave like a direct-gap semiconductor, as regards the TQC level system, exhibiting discrete absorption and emission bands. Additionally, we report for the first time multiple exciton generation in Si nanofilms, previously observed in nanodots only [7], and a working prototype Si–SnO_2 photovoltaic cell that employs multiple exciton generation. Note that multiple exciton generation has been pursued as a possible path to achieve improved efficiency and reduced costs of photovoltaic solar power installations.

Further on, we shall avoid the use of the term "quantum well" to describe the discrete level system generated by the TQC in semiconductor nanofilms, as this term is commonly used to describe the relatively small energy changes of the valence and conduction bands in the semiconductor zone structure occurring due to dimensional effects (see, e.g., [8]), with the zone structure itself generated over the two in-plane dimensions of the film, whereas the presently described TQC level system seems to have been largely overlooked by the semiconductor physics community, until now. The main reason for this was probably an impression that such phenomena are only observable by photoemission spectroscopy in epitaxial systems. Another possible reason is that the simple estimates [15] for the presence and observability of the confinement effects based on the free-electron mass are much off the target for most materials, where the effective electron mass is much smaller than m_o, misleading and discouraging the researchers.

Note that the presently reported spectral transitions refer to the TQC electron movement quantized in the direction normal to the film, therefore the effect of the film thickness on the state energies is strong, with transition energies achieving the work function of the material. Note also that the presently reported spectral features are common for semiconductors and metals, with the material-specific properties expressed in the simple model by a single parameter, the effective electron mass, while showing no direct dependence on other parameters such as the band gap of the material, compare to our results obtained in metal films [14]. On the other hand, the term "quantum well" is associated to semiconductor heterostructures with layers of nanometer thickness, with the properties of these quantum wells dependent both on the layer thickness and other essential properties of the semiconductors, such as the band gap [16]. Thus, presently we describe the TQC as an isolated phenomenon occurring in individual materials.

2. Experimental

Fused silica substrates 25 mm in diameter and 1 mm thick (Esco Optics) were used to deposit the films. Commercial Si and SnO_2 (Sigma/Aldrich) were used to produce nanocrystalline films on a commercial sputtering/thermo-evaporation Benchtop Turbo deposition system (Denton Vacuum). The substrate temperature was 475 °C in all experiments. The film thickness was controlled by XRD [9], with the XPert MRD system (PANalytic) calibrated with standard nanofilms of the same materials. The estimated absolute uncertainty of film thickness was 2.5%; the relative uncertainties were much smaller, determined by the shutter opening times of the deposition system. AFM images were obtained on a commercial AFM system (Agilent Technology, 5500 AFM/SPM).

Absorption and emission spectra were recorded on a Hitachi U-3900H UV–Visible Spectrophotometer and an Edinburgh Instruments FS5 Spectrofluorometer. The absorption spectra in the near-IR were recorded on a PF 2000 FTIR spectrometer (Perkin Elmer). The spectral peak maxima were precisely located using the PeakFit software (Sigmaplot). Polynomials were fitted and fitting uncertainties estimated using the LINEST function in Excel (Microsoft).

Photoelectric current response measurements were carried out using a high-pressure Xe lamp ($W = 1000$ W; Ariel Corporation, Model 66023), a monochromator (Thermo Jarrell Ash, Mono Spec/50), a DET10A Si Biased detector (THORLABS, supplied with the spectral