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Quantum confinement in metal nanofilms: Optical spectra

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ABSTRACT

We report optical absorption and photoluminescence spectra of Au, Fe, Co and Ni polycrystalline nanofilms in the UV–vis–NIR range, featuring discrete bands resulting from transverse quantum confinement. The film thickness ranged from 1.1 to 15.6 nm, depending on the material. The films were deposited on fused silica substrates by sputtering/thermo-evaporation, with Fe, Co and Ni protected by a SiO_2 film deposited on top. The results are interpreted within the particle-in-a-box model, with the box width equal to the mass thickness of the nanofilm. The transverse-quantized energy levels and transition energies scale as the inverse square of the film thickness. The calculated values of the effective electron mass are 0.93 (Au), 0.027 (Fe), 0.21 (Co) and 0.16 (Ni), in units of m_o – the mass of the free electron, being independent on the film thickness. The uncertainties in the effective mass values are ca. 2.5%, determined by the film thickness calibration. The second calculated model parameter, the quantum number n of the HOMO, was thickness-independent in Au (5.00) and Fe (6.00), and increased with the film thickness in Co (from 7 to 9) and Ni (from 7 to 11). The transitions observed in the absorbance all start at the level n and correspond to $\Delta n = +1, +2, +3$, etc. The photoluminescence bands exhibit large Stokes shifts, shifting to higher energies with the increased excitation energy. The photoluminescence quantum yields grow linearly with the excitation energy, showing evidence of multiple exciton generation. A prototype Fe–SnO_2 nanofilm photovoltaic cell demonstrated at least 90% quantum yield of photoelectrons at 77 K.

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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, respectively [1,2].

Quantum well structures exhibiting quantum confinement effects were investigated in metal nanofilms with a well-defined number of atomic monolayers deposited on single-crystal substrates, and studied mostly by angle-resolved photoemission in vacuum. These measurements were predominantly performed for the electrons with binding energies not exceeding 2–3 eV, and the 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].

Earlier we reported indirect evidence for the one-dimensional transverse quantum confinement (TQC) in conductive and semi-conductive nanofilms, observed via exchange anticrossing spectra in nanosandwich structures [4]. Recently we reported direct spectral evidence for TQC in Si and SnO_2 semiconductor nanofilms [5]. Presently we report direct evidence for TQC in Au, Fe, Co and Ni nanofilms, in the form of their UV–vis–NIR absorption and emission spectra.

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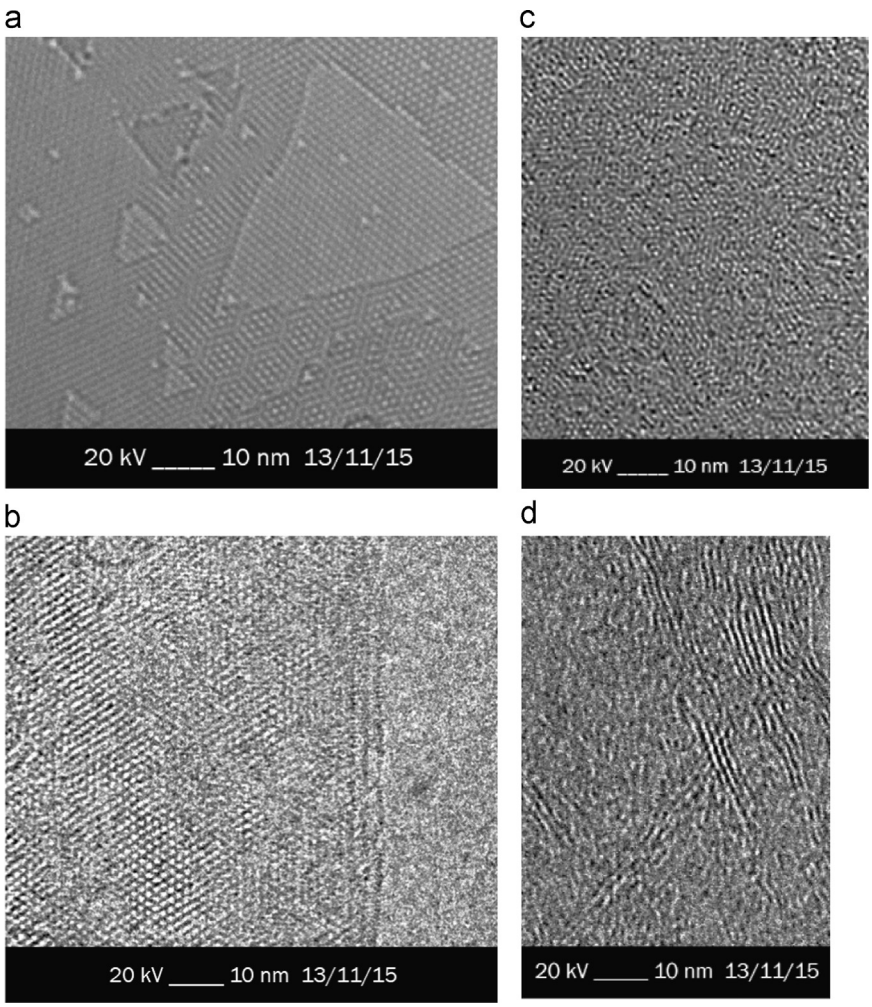

Fig. 1. SEM images of selected metal nanofilms used in the study: (a) Au 1.1 nm thick; (b) Fe 7.8 nm thick, (c) Co 7.3 nm thick; (d) Ni 5.3 nm thick.

2. Experimental

Fused silica substrates 25 mm in diameter and 1 mm thick (Esco Optics) were used to deposit nanocrystalline metal films. Commercial Au, Fe, Co and Ni (Sigma/Aldrich) were used to produce nanofilms on a commercial sputtering/thermo-evaporation Benchtop Turbo deposition system (Denton Vacuum). The substrate temperature was 475 °C, unless stated otherwise. The film thickness was controlled by XRD [6], with the XPert MRD system (PANalytic) calibrated by 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. Protective SiO_2 nanofilms were produced by pulsed laser deposition (CO_2 laser; 5 J/pulse) at 750 °C [7]. The films were of homogeneous thickness, with less than 2% variation from the center to the edges, and the central 5 mm were used in the spectral measurements.

SEM images of the nanocrystalline metal films were recorded on a High-resolution field-emission JSM-7500F SEM (JEOL), with the selected images shown in Fig. 1.

The 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 located using PeakFit (Sigmaplot). The second-order polynomials were fitted and the fitting uncertainties estimated using the least-squares method implemented in the LINEST function (Microsoft Excel).

The 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), and a model 2182A nanovoltmeter (Keithley Instruments), all connected to a computer via GPIB interface, controlled by home-made software in the LabView programming environment (National Instruments).

The low-temperature measurements were carried out at 77 K using an Optistat DN-V2 optical cryostat (OXFORD