Optical study of monolayer, few-layer and bulk tungsten disulfide

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Semiconducting transition metal dichalcogenides (TMDCs) such as MoS_2, $MoSe_2$, WS_2, or WSe_2 have recently attracted a lot of attention due to their unique electronic structures and optical properties. When thinned down to a monolayer, TMDCs transform from indirect- to direct-bandgap semiconductors and exhibit a number of intriguing optical phenomena such as valley-selective circular dichroism, doping-dependent charged excitons, or strong photocurrent response.

Here, we report a comprehensive study of the optical properties of thin films of WS_2 with thicknesses ranging from monolayer (1 ML) to octalayer (8 MLs) and of a bulk flake, carried out in a wide temperature range (5-300 K) using micro-photoluminescence (μ-PL) and micro-reflectance contrast (μ-RC) spectroscopy techniques.

The indirect- to direct-bandgap transformation is observed in the μ-PL experiment at liquid helium temperature as the layer thickness is being reduced down to an 1 ML. In terms of quantity, the emission intensity increases by 4 orders of magnitude when the flake thickness is being decreased from 8 MLs to 1 ML. The μ-PL spectrum of the 1 ML emerges at about 2.0 eV and displays several well-resolved emission peaks with the broadenings on the order of ∼10 meV, which are associated with the recombination of direct excitons (neutral, charged and localized/bound) formed at the K point of the Brillouin zone. Moreover, at low excitation power (∼1 μW) the μ-PL from the 1 ML is dominated by a broad emission band extending from about 1.65 eV to the main signal occurring at ∼2.0 eV. We tentatively ascribe this emission to the donor-acceptor pair recombination. The indirect-related emission shifts to lower energy with increasing the flake thickness, from ∼1.7 eV for the 2 ML flake to ∼1.4 eV for the 8 ML flake, which is a consequence of a simultaneous reduction of the fundamental bandgap. Due to opposite types of temperature behaviour (redshift and blueshift), we claim that the indirect recombination processes involve two different valleys in the conduction band, K and Λ, and the same valley in the valence band, Γ. For 2 MLs and 3 MLs, we demonstrate that a thermally-driven crossover from indirect to direct transitions that occurs when a sample is heated up from 5 K to 300 K.

We also study the effect of thickness on the excitonic resonances with the aim of μ-RC measurements. Our results display three main features, which we associate with the absorption of light by A, B, and C excitons. The features related to A and B excitons display only a weak sensitivity to the number of layers, while the energy of the C resonance quickly decreases with increasing the film thickness. Moreover, in the case of the 1 ML, apart from typically observed the neutral and charged exciton-related resonances within the A exciton, we show a new feature which is attributed to the absorption light by a localised/bound exciton. For flakes thicker than 1 ML, we demonstrate that the A exciton resonance exhibits a double structure, which has not been reported so far.