

高効率太陽電池・光触媒開発のための 酸化物半導体に於けるキャリアダイナミクスの解明

Carrier Dynamics in Oxide Semiconductors
for the Development of High Efficiency Solar Cells and Photocatalysts

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Zinc oxide (ZnO) is a transparent semiconductor crystal with a wide bandgap and has attracted huge attention for its optoelectronic applications, such as blue and ultraviolet (UV) light-emitting diodes, high efficiency solar cells, and photocatalysts. Under an ambient condition, a recombination of a loosely bound electron-hole pair, i.e., a free exciton (FX), contributes the photoluminescence (PL) in the UV energy range. Since the binding energy of the FX is 60 meV and exceeds the thermal energy at room temperature, the dynamical behavior of FXs governs the PL process and thus controls the performance of actual applications. The dynamics of FX can be approached by monitoring temporal profiles of the PL in the near-band edge (NBE) emission range.

In this study, time-resolved PL experiments on ZnO crystals have been conducted at room temperature to elucidate the FX dynamics and origins of the NBE emission. Biexponential decay functions well reproduce the temporal profiles of the PL spectra, indicating that two origins with different decay times contribute to the NBE emission. By introducing the FX-longitudinal optical (LO) phonon interactions into the analysis of the PL spectra, stronger FX-LO phonon coupling for the fast decay than for the slow decay has been clarified. Moreover, reduction in an FX PL (zero-LO phonon emission) is found to be much larger in the slow decay than in the fast decay. These results suggest that the NBE emission with the fast decay occurs near the crystal surface, while the slow one happens inside the bulk.

研究目的

酸化物半導体を用いた高効率太陽電池材料や光触媒材料の開発において、光吸収によって形成される励起電子と正孔のキャリアダイナミクスの詳細な理解が重要となる。特に酸化亜鉛 (ZnO) は化学的に安定な透明酸化物半導体であり、直接遷移型のギャップを有することから、高効率光応答デバイスとして期待されて

いる。ZnOにバンドギャップを超えたエネルギーを有する光を照射することで励起された電子と正孔による励起子が形成される。室温でのデバイス応用を考える上で、この励起子のダイナミクスの解明が欠かせない。励起子の再結合時に放出される発光スペクトルの時間変化を調べることで励起子のダイナミクスを間接的に計測することができる。そのため、これまでZnOに形成される励起子の再結合過程を明らかにす

るため、多くの時間分解発光研究が展開され、励起子由来の発光には緩和時間の異なる2種の発光現象が存在することが報告されている。しかしながら、それぞれの発光起源について統一的な理解が得られていない。そこで本研究では緩和時間の異なる2種の発光起源を明らかにするため、励起子-格子相互作用を取り入れたモデルを用いて時間分解発光スペクトルの詳細な解析を行った。

概 要

Zinc oxide (ZnO) is a transparent semiconductor crystal with a wide bandgap, $E_g = 3.37$ eV at room temperature, and has attracted huge attention for its optoelectronic applications, such as blue and ultraviolet light-emitting diodes, high efficiency solar cells, and photocatalysts. Under an ambient condition, a recombination of a bound electron (e)-hole (h) pair, a free exciton (FX), contributes the photoluminescence (PL) in the UV energy range. Since the binding energy of the FX is 60 meV and exceeds the thermal energy at room temperature, the dynamical behavior of FXs governs the PL process and thus controls the performance of actual applications. The FX dynamics have been experimentally examined by probing temporal variations of the PL by using the pump-probe method. The PL energy of a high purity ZnO crystal, ~ 3.3 eV, shows good agreement with the difference between the E_g and the FX binding energy, and thus, this PL is often called a near-band edge (NBE) emission.

The intrinsic lifetime of the FX emission, obtained in a high purity ZnO crystal, is longer than the nanosecond order. However, it has been reported that the PL process mostly completes

in much shorter times (< 1 ns) and the process consists of a number of PL origins with different decay times, and thus the relaxation process of the photoexcited electrons that governs the PL lifetime is rather complicated. The depopulation rates of the photo-excited carriers, which determine the lifetime of the NBE PL, have been discussed in terms of the e-h recombination at impurities and/or defects whose energy levels are located within the ZnO band gap. In spite of the former efforts, a proper understanding of the extrinsic channels during the PL process and their influences on the FX dynamics, which are necessary to develop ZnO optoelectronic devices, is not obtained yet.

In this study, time-resolved experiments on a ZnO single crystal have been performed in picosecond order to clearly the NBE PL process of ZnO. The intensity decay of the PL in the ZnO crystal is found to be much complicated; it was not possible to fit the time-dependent intensity using a single exponential function. Furthermore, the shape of the decay curve is found to change significantly by energy. This spectral change was well fitted by a function which is an extension of the intensities and lifetimes of the biexponential decay function to be the energy-dependent values. The obtained lifetimes were determined to be 20 ps and 80 ps for the fast and slow decays, respectively. The spectral area of the emission peak of the slow decay is about 1.6 times larger than that of the fast process. These results indicate that the fast decay is much governed by the impurity-induced recombination process, compared to the slow one.

Asymmetric shapes of both the fast and

slow PL spectra were found to be derived by FX-longitudinal optical (LO) phonon interactions. By fitting the spectra incorporating the interaction, stronger FX-LO phonon coupling for the fast decay than for the slow decay has been clarified. Moreover, reduction in an FX PL (zero-LO phonon emission: I_0) is found to be much larger in the slow decay than in the fast decay. The smaller value of I_0 can be understood in terms of the re-absorption process of photons inside the crystal. These results suggest that the NBE emission with the fast decay occurs near the crystal surface, while the slow one happens inside the bulk.

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