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Nearly temperature-independent ultraviolet light emission intensity of indirect excitons in hexagonal BN microcrystals

Shigefusa F. Chichibu,[1,a)] Youichi Ishikawa,[1] Hiroko Kominami,[2] and Kazuhiko Hara[2]
[1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980–8577, Japan*
[2]*Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8011, Japan*

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The radiative performance of hexagonal boron nitride (h-BN) was assessed by the spatio-time-resolved luminescence measurements on its microcrystals (MCs) annealed in an O_2 gas ambient. The MCs exhibited distinct deep ultraviolet luminescence peaks higher than 5.7 eV, although h-BN is an indirect bandgap semiconductor. The result indicates a strong interaction between the indirect excitons (iXs) and LO/TO (and LA/TA) phonons at T points of the Brillouin zone. Such phonon replicas of free iXs and a luminescence band at 4.0 eV showed negligible thermal quenching, most probably assisted by the strong excitonic effect, enhanced phonon scattering, and formation of a surface B_xO_y layer that prevents excitons from surface recombination by the thermal excitation. Conversely, the luminescence band between 5.1 and 5.7 eV, which seems to consist of LO/TO phonon replicas of iXs localized at a certain structural singularity that are further scattered by multiple TO phonons at K points and another two emission peaks that originate from the singularity, showed the thermal quenching. In analogy with GaN and AlGaN, cation vacancy complexes most likely act as native nonradiative recombination centers (NRCs). In the present case, vacancy complexes that contain a boron vacancy (V_B), such as divacancies with a nitrogen vacancy (V_N), V_BV_N, are certain to act as NRCs. In this instance, iXs delocalized from the singularity are likely either captured by NRCs or the origin of the 4.0 eV-band; the latter is assigned to originate from a carbon on the N site or a complex between V_B and an oxygen on the N site. *Published by AIP Publishing.*
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I. INTRODUCTION

Different from classical wurtzite structure group-III nitride semiconductors, such as AlN, GaN, and InN, hexagonal boron nitride (h-BN) crystallizes in layers of a two-dimensional (2D) honeycomb structure based on three sp^2 covalent bonds that are connected by an out-of-plane π bond, and the bulk h-BN consists of few- to multilayer crystals and flakes. Therefore, h-BN exhibits unique properties: because of the van der Waals bond, monolayer h-BN can be a platform for the growth of graphene and other 2D material heterostructures.[1] Since the bandgap energy (E_g) of h-BN is approximately 6 eV (Ref. 2) and Watanabe *et al.*[3] reported a lasing action of high crystalline quality h-BN bulk single crystals in the deep ultraviolet (DUV) wavelength region at approximately 5.77 eV (215 nm), h-BN has become one of the promising semiconductors for DUV and ultraviolet (UV) light emitters. In addition to the single crystalline bulk crystals, powders and microcrystals (MCs) of h-BN are candidates of UV light emitters: a plane-emission DUV lamp operating at 225 nm was demonstrated by using a field-emission array as an electron source,[4] and the strong cathodoluminescence (CL) band at approximately 320 nm (Refs. 5–10) from annealed h-BN MCs[10] has been considered for the application to an UV light-emitting phosphor.

However, because the growth of high-quality h-BN crystals[3,7] is still difficult, consensus has not yet been established even for the fundamental material properties. With respect to the fundamental bandgap, for example, there has been a strong contrast between *ab initio* calculations,[11–14] which predicted an indirect bandgap, and optical experiments that indicated a direct bandgap.[3,15,16] By using two-photon excitation experiments, Cassabois *et al.*[2] recently concluded that h-BN has an indirect bandgap with E_g of 5.955 eV at 10 K. Their explanation was that indirect excitons (iXs) built from M and K points of the Brillouin zone (BZ) for the conduction and valence bands [E_C(M) and E_V(K)], respectively,[11–14] require the scattering by phonons of proper wavevector **MK** to fulfill momentum conservation during photon emission or absorption. According to the phonon dispersion of h-BN,[17,18] the near-band-edge (NBE) five doublet emission peaks at approximately 5.93, 5.89, 5.86, 5.79, and 5.76 eV (Ref. 2) were assigned to the ZA(T), TA(T), LA(T), TO(T), and LO(T) phonon replicas of iXs [$X_{ZA(T)}$, $X_{TA(T)}$, $X_{LA(T)}$, $X_{TO(T)}$, and $X_{LO(T)}$], respectively, where the notation T in parentheses represents the T points in the middle of the first BZ. The reason why such phonons were required can be understood by simple geometrical consideration of the hexagonal BZ, where the phonons with wavevector **MK** (equivalent to **ΓT**) are required for the iXs to interact with photons by the phonon scattering process. As well as the NBE emission, origins of a so-called defect-originated luminescence band between 5.1 and 5.7 eV (5.5 eV-band)[19–24] and the oxygen-enhanced luminescence band at approximately 4.0 eV (4.0 eV-band)[5–10] remain controversial. Cassabois *et al.*[24] assigned the 5.5 eV-band as

a)E-mail: chichibulab@yahoo.co.jp