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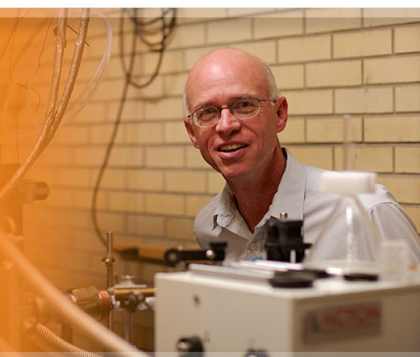
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Intercalation of hexagonal boron nitride with potassium

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We have performed photoluminescence, photoexcitation, and transmission electron microscopy measurements on boron nitride films grown by chemical vapor deposition and later reacted with potassium. After reaction, the potassium atoms were found to intercalate the BN host and to form a $(2 \times 2)R 0^\circ$ in-plane structure which is commensurate with the pristine BN lattice. Optical transitions with ~ 2.7 eV onsets were found to occur within the ~ 5 -eV BN band gap and have been interpreted as Γ -point transitions between the K(4s) band and the BN(2p) bands. The absence of an appreciable shift in the E_{2g} phonon frequency of the pristine and reacted films suggests that the charge transfer between the K and BN bands is very small.

I. INTRODUCTION

The propensity for hexagonal graphite to form intercalation compounds through reactions with many atomic and molecular species is well known and reasonably well understood. Graphite intercalation compounds (GICs) are formed by the insertion (or intercalation) of the reacting species between the strongly bonded sheets of carbon atoms, taking advantage of the much weaker interlayer bonds. Because of its structural similarity to graphite, hexagonal boron nitride (hBN) was thought to be another likely host for intercalation. However, the intercalation of hBN has proven to be considerably more difficult than graphite, and many contradictory findings have been reported in the literature. In this work, we report conclusive evidence for the intercalation of potassium into a hBN host.

Except for the layer stacking, the structures of graphite and hBN are similar. The in-plane bond length and interlayer separation of hBN are the same as graphite to within a few percent.¹ The bonding energies are also similar. However, while pristine graphite is a semimetal, hBN is a wide gap insulator. Experimentally determined values of the hBN band gap have been reported to range from 3.2 to 5.8 eV,²⁻¹¹ while band-structure calculations estimated values of the band gap from 2.45 to 12.7 eV.⁵⁻¹⁷ The majority of experimental evidence, however, seems to agree on a value near 5.2 eV for the band gap.¹¹

Since the early attempts to intercalate BN by Croft,¹⁸ there have been many reports regarding efforts to synthesize intercalation compounds using a hBN host.¹⁹⁻²⁶ A comprehensive review of these efforts was given recently by Sakamoto, Speck, and Dresselhaus²⁶ and will not be repeated

here. Of particular relevance to the present work, however, are the reports of alkali metal reactions with hBN. Freeman and Larkindale²⁰ reacted white BN powder with Li, Na, and K. Whereas no reaction was observed for the case of Li, reactions with Na and K produced dark grey and buff colored substances, respectively. Further investigation of the K-reacted material revealed an approximate stoichiometry of $(\text{BN})_{13}\text{K}$ and x-ray lines with a periodicity of 4.4 Å, which were absent in the pristine powder, appeared subsequent to the reaction. Mugiya *et al.*²¹ reacted white BN powder with Na, K, and Cs, and reported that the alkali metal-BN complexes displayed a marked catalytic activity for para-ortho-hydrogen conversion and hydrogen-deuterium equilibration similar to the case of the low-stage alkali metal graphite compounds.²⁷ Sakamoto *et al.*²⁶ reacted Cs with a highly oriented, transparent, pyrolytic BN flake and observed no evidence of a systematic intercalation; however, TEM observations suggested intercalation islands were formed by the introduction of Cs.

II. MATERIALS PREPARATION AND CHARACTERIZATION

In this study, BN films were obtained by a chemical vapor deposition (CVD) process using silica substrates. The film thickness was estimated from scanning electron microscopy (SEM) measurements to be ~ 1 – 2 μm . Further SEM measurements revealed that the films possessed a layered morphology similar in appearance to pyrolytic graphite, but with much smaller grain sizes. The as-deposited films had a yellow tint but were otherwise transparent. Whereas the yellowish tint has been associated with crystalline defects in hBN,²⁸ the overall transparency arises from the 5-eV band gap. The $T = 300$ K Raman spectrum of the pristine BN film is shown in Fig. 1. Radiation (4880 Å) from a Spectra Physics 164 argon-ion laser with light polarized perpendicular to the BN \hat{c} axis ($\mathbf{E} \perp \hat{c}$) was used to excite the high-frequency E_{2g} intralayer phonon mode. (This mode is shown schematically in the figure.) The frequency of the Raman

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line observed in Fig. 1 is 1361 cm^{-1} and is in agreement with values reported by other workers.²⁹ The full width at half maximum (FWHM) intensity of the 1361-cm^{-1} line is $\sim 32\text{ cm}^{-1}$. The position and the width of the 1361-cm^{-1} line have been shown^{30,31} to vary linearly with inverse crystallite size (basal-plane dimension), which is a sensitive measurement of the crystalline order. The E_{2g} peak downshifts by $\sim 8\text{ cm}^{-1}$ and the FWHM decreases from 40 to 9 cm^{-1} as the basal-plane crystallite size varies from 35 to 500 Å . Using this criterion, we estimate the average basal-plane crystallite diameter of the CVD BN samples to be $\sim 50\text{ Å}$.

To carry out the reaction with potassium, the BN films were loaded in a pyrex ampoule with high-purity K, evacuated to 10^{-6} Torr, sealed, and placed in a two-zone furnace. The temperatures of the BN and K were held at 220 and 200°C , respectively, for 24 h. After removing the ampoule from the furnace, the BN films had changed to a violet color, indicative of a strong optical absorption occurring in the visible region of the spectrum; this strong optical absorption was absent in the pristine films. Because of the reactivity of K with O_2 and H_2O , the K-BN films were handled in an argon atmosphere dry box having less than 5 ppm O_2 .

Experiments probing the structure are required to establish whether the K-BN materials are intercalation compounds or if the K atoms occupy random defect sites within the BN lattice. Due to the small film thickness ($\sim 1\text{--}2\text{ }\mu\text{m}$), we were unable to observe x-ray diffraction lines from either the pristine or the K-reacted samples. Transmission electron microscopy (TEM) has been shown to be a complementary technique to x-ray diffraction for probing the structure of acceptor-type and some low-stage donor-type GICs.³² TEM is especially well suited for the K-BN films since the TEM electron diffraction patterns probe the sample structure on a $\sim 1\text{-}\mu\text{m}$ scale. The electron diffraction pattern of a K-BN sample is shown in Fig. 2(a) accompanied by a schematic identification of the BN and K spots in Fig. 2(b). The Bragg reflections are spread into disks because a convergent beam was used to form the diffraction pattern. However, the arrangement of the spots clearly show that the K atoms occupy a $(2\times 2)R\ 0^\circ$ superlattice which is commensurate with the

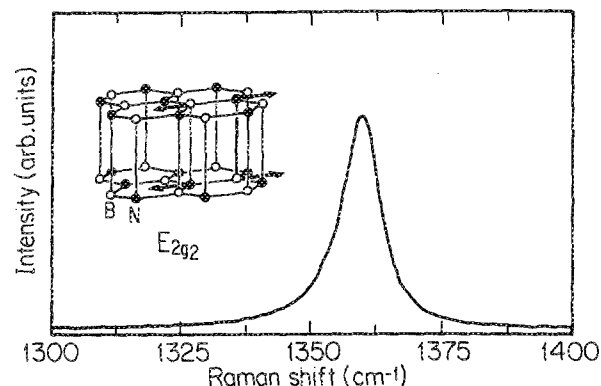
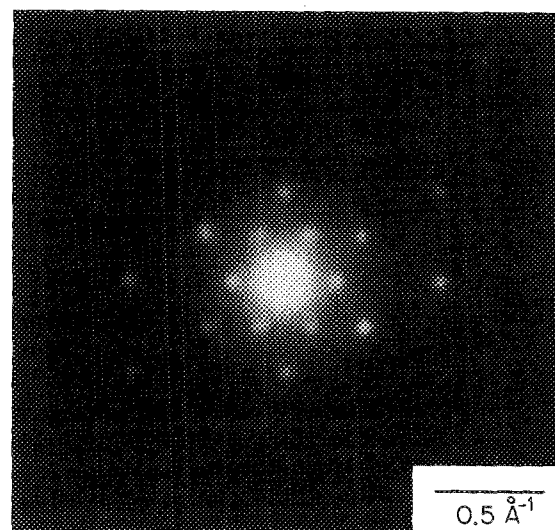
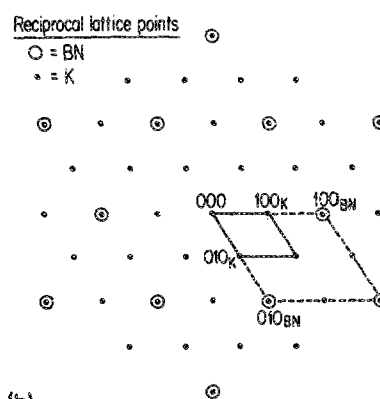


FIG. 1. Raman spectrum of a pristine CVD-grown BN film and the E_{2g} normal mode (shown in the inset). The frequency and width of the phonon line shape provides information concerning the in-plane order of the material.



(a)



(b)

FIG. 2. In-plane structural characteristics of a K-BN film obtained from TEM measurements. The arrangement of the K atoms in (a) is found to be commensurate with the BN lattice and form a $(2\times 2)R\ 0^\circ$ structure which is apparent in the schematic diagram (b).

hBN lattice. This in-plane arrangement is typical of stage 1 C_8M GICs (where $\text{M} = \text{K}, \text{Rb}, \text{Cs}$) and of some ternary GICs (e.g., stage 1 C_4KHg).³² Due to the reactivity of the K-BN films we only briefly observed the $(2\times 2)R\ 0^\circ$ structure in the microscope prior to deintercalation. Additionally, we were unable to observe the interplanar structure (i.e., the separation and stacking sequence of the BN and K layers along the c axis); however, the observation of the commensurate K superlattice provides strong evidence for intercalation. It should be mentioned that adsorbed monolayer of alkali metals on hexagonal substrates also form commensurate superlattices, although in that case the structure is usually $(\sqrt{3}\times\sqrt{3})R\ 30^\circ$ and exists only under ultrahigh vacuum conditions. The association of the $(2\times 2)R\ 0^\circ$ potassium superlattice with an adsorbed species is not likely at the modest vacuum levels of the present experiment. If the K atoms intercalate the BN layers in a periodic manner (as was found²⁵ to be the case for BN-BiCl_3) and there are n layers of BN separating adjacent layers of K, we estimate the stoichiometry of our BN-K compound as $(\text{BN})_{4n}\text{K}$ from the planar arrangement of the K, B, and N atoms.

The ability of hBN to intercalate guest species seems to be intimately tied to the degree of crystallinity of the host material. Well-ordered hBN such as pyrolytic boron nitride has been shown to react very slowly with alkali metals,²⁶ whereas less ordered materials such as hBN powders^{20,21} react much more readily. The crystallinity of the BN films used in this study is of the same order as the BN powders used in previous studies.²⁶

Attempts to measure the Raman spectrum of the K-BN films with the 4880-Å laser line proved unsuccessful because of an intense photoluminescence spectrum (see Fig. 3) which arose subsequent to the reaction. The room-temperature ($T = 300$ K) photoluminescence spectrum (PL) produced with a 4579-Å excitation line is shown in Fig. 3. The spectrum suggests the occurrence of phonon-assisted electronic transitions since the peaks in the PL spectrum are periodic in the frequency of the BN E_{2g} phonon (i.e., 1360 cm^{-1}). These data are similar to PL spectra obtained on semiconductors with deep-level transitions (e.g., CuGaAs).³³

OPTICAL RESULTS

Optical transitions in the K-BN films can also be observed from the photoexcitation (PE) spectrum (Fig. 4). In this experiment, the luminescence intensity is measured as a function of the wavelength of the incident light. The spectrum indicates that the onset of luminescence begins near 460 nm or ~ 2.7 eV, which would coincide with the onset of electronic transitions. The electronic transitions undoubtedly involve transitions between the K(4s) intercalant band and one or both of the BN(2p) bands. The onset energy measured in this way places the K(4s) band nearly in the center of the ~ 5.2 -eV BN band gap. At longer wavelengths, peaks in the intensity, periodic in the BN phonon energy, are evident as was the case in Fig. 3.

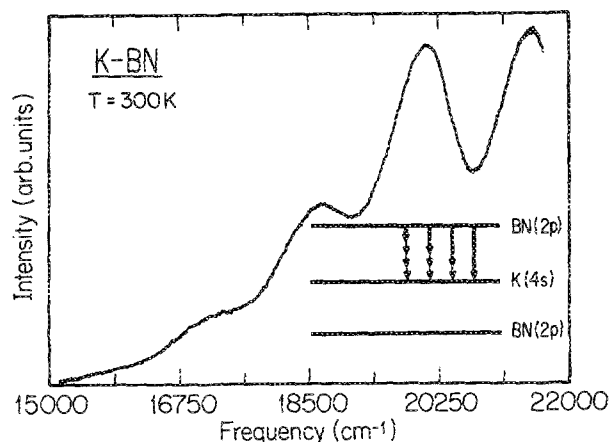


FIG. 3. Photoluminescence (PL) spectrum of a K-BN film obtained using 4579-Å laser excitation. The peaks indicate that phonon-assisted electronic transitions occur within the 5.2-eV BN band gap. The threshold energy for the luminescence occurs near 2.7 eV. Electronic transitions which may be responsible for the peaks in the luminescence are shown schematically in the inset (lower right). The uppermost arrows represent the electronic and experimentally observed transitions, while the short arrows correspond to the characteristic energy of the multiphonon process.

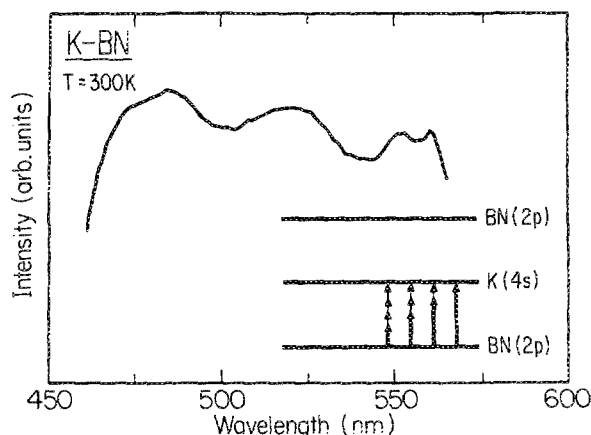


FIG. 4. Photoexcitation (PE) spectrum of a K-BN film. The onset for optical transitions occurs near 2.6 eV (480 nm). The inset shows a schematic representation of phonon-assisted electronic transitions which would produce the PE spectrum where the lowermost and short arrows represent the energies of the electronic and phonon contributions to the optical transition, respectively.

Optical transitions which would produce the peaks in the luminescence intensity of Figs. 3 and 4 are shown schematically in the insets to the figures. The long and short arrows represent the energies of the electronic ($q = 0$) and phonon-assisted ($q \neq 0$) components, respectively. Although the transitions shown in these insets involve the excitation of electrons from the K(4s) band to the BN(2p) conduction band, the transitions could just as well involve the production of holes in the BN(2p) valence band. According to this model, the Fermi level (E_F) lies in the K(4s) impurity band. Although the exact location of E_F within the impurity band is not known, it is reasonable to assume that the 4s band is half filled. For the PL experiment illustrated in Fig. 3, electrons are excited from the K(4s) band to the BN(2p) band with 2.7-eV light and the peaks in the spectrum arise from the decay of these excited electrons to their ground state. The purely electronic transition represents the highest-energy peak (2.7 eV) and corresponds to the minimum energy separation of the bands for direct transitions. The energies of the remaining transitions are reduced by multiples of the BN E_{2g} phonon energy (1361 cm^{-1} or $\sim 0.17\text{ eV}$), as observed in the experiment. In the PE process shown in Fig. 4 the luminescence intensity arises from the excitation of electrons from the lower to the upper band as the energy of the exciting light is increased. The electronic onset energy measured in this fashion is 2.6 eV, slightly less than that observed in the PL measurement. Since the energies of the PL and PE onsets add to equal the energy of the pristine BN band gap, it is strongly suggestive that the PL and PE measurements are probing different transition processes. That is, the PL experiment may be probing the transitions between the K(4s) band and the BN(2p) conduction band while the PE measurement is more sensitive to transitions between the BN(2p) valence band and the K(4s) band.

The in-plane arrangement of the K atoms, the enormous intensity of the PL and PE spectra, and the multiphoton relaxation processes all argue in favor of an impurity band

picture instead of a collection of localized states. If the K species gives rise to a donor compound as it does in the case of graphite, we may expect some or all of the K(4s) electron to be transferred to the BN(2p) conduction band. In the case of GICs, this charge transfer results in an expansion of the in-plane carbon-carbon bond length and a softening of the high-frequency, Raman-active E_{2g} phonon.³⁴ Since the multiphonon processes observed in Figs. 3 and 4 yield a phonon frequency unchanged from its value in the pristine state, the charge transfer from the K(4s) to a BN(2p) band is inferred to be small. This is understandable given the large energy separation of the BN(2p) bands from the Fermi level in pristine BN.

We now turn our attention to the origin of the optical transitions responsible for the intense photoluminescence observed in Fig. 3. We have reproduced the two-dimensional (2D) tight-binding calculation of the BN(2p) bands by Doni and Parravicini¹² along high symmetry directions in Fig. 5. The corresponding 2D Brillouin zone is shown in the inset. The results of the PL and PE experiments indicate that the K(4s) impurity band is located nearly in the center of the BN(2p) bands. In the band representation shown, a high joint density of states which will yield transitions between the K(4s) band and a BN(2p) band with energy onsets of ~ 2.6 – 2.7 eV cannot occur at the zone center (Γ point) but are more likely to occur at the M or K points. However, if we incorporate zone folding caused by the $(2 \times 2)R 0^\circ$ superlattice, in which case the M point is folded to the Γ point, allowed optical transitions can occur at the zone center with energies consistent with the measured transition onsets. Phonon-assisted transitions are likely to occur as k moves away from the Γ point.

In summary, we have reacted K with CVD-grown BN films to produce K-BN intercalation compounds. The K atoms were found to occupy a $(2 \times 2)R 0^\circ$ superlattice which is commensurate with the BN lattice. The reduced zone scheme obtained by the zone folding associated with the in-plane structure was found to support optical transitions near

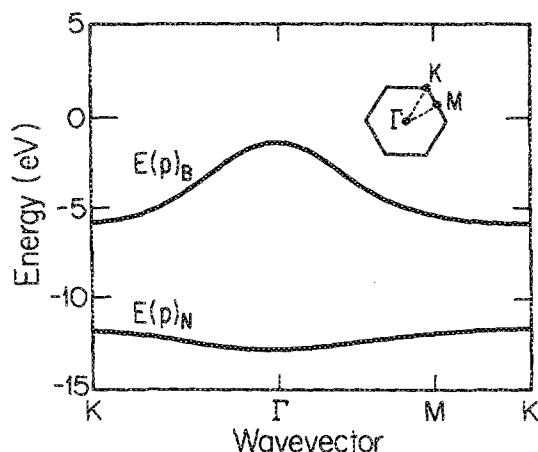


FIG. 5. 2D BN(2p) bands from Ref. 12 are plotted in the extended zone scheme. The 2D Brillouin zone is shown in the inset with the principal symmetry points labeled.

the zone center with onset energies consistent with onsets measured by photoluminescence and photoexcitation measurements. The frequency of the BN E_{2g} phonon involved with the phonon-assisted optical transitions was unchanged from its value in the pristine state. This was interpreted as evidence supporting weak charge transfer from the K(4s) electrons to a BN(2p) band. Taken collectively, these results indicate that K forms a band within the ~ 5 -eV BN band gap to produce a compound structurally similar to graphite intercalation compounds. Although we know of no prior measurements of the transport properties of these compounds, the K-BN compounds are expected to exhibit novel low dimensional electronic and thermal properties which are characteristic of the host.

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