Anisotropic optical properties of hexagonal boron nitride films

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Abstract. A study is performed of the transmission, reflection, and photoluminescence spectra of films of hexagonal boron nitride with the thickness of several mono-atomic layers prepared by splitting bulk samples in an ultrasonic bath. The homogeneity of the obtained samples is established via scanning electron microscopy. Spectral dependences of the linear and circular polarizations of light transmitted through a sample are measured. Studying the Stokes parameters of light transmitted through a sample allows latent anisotropy in the optical properties of boron nitride films to be identified. Statistical analysis of optical microscope images reveals a macroscopic particle density distribution with ordering that corresponds to the optical axis observed in polarization.

Introduction

Interest in atomically thin (2D) materials has grown exponentially since reports of the unique properties of graphene were first published. Researchers have expanded the family of known 2D materials to include, e.g., the MXene class of two-dimensional inorganic compounds, transition metal dichalcogenides (TMDs), and boron nitride (BN). The diverse properties of 2D materials and their ultrathin nature open up the prospect of creating van der Waals hetero- structures in which different two-dimensional materials are stacked in layers [1], and offer the possibility of forming heterostructures with huge potential. Due to the strong covalent bonds within layers and relatively weak bonds between them, such structures retain many of the properties of the original materials and can also acquire completely new properties. Due to the weak van der Waals coupling between layers, we need not worry about matching the lattice parameters when creating heterostructures. This allows us to use the entire range of two-dimensional materials, regardless of the value of the lattice constant.

Two-dimensional materials can be synthesized in two fundamental ways: top-down and bottom-up. Using such bottom-up techniques as chemical vapor deposition or molecular beam epitaxy, we can produce high-quality 2D materials over relatively large areas, but they are labor-intensive, energy-intensive, and expensive. Top-down means include bulk crystal delamination. The simplest and most common technology for peeling bulk crystals is the mechanical splitting of layers using adhesive tape, so-called Scotch technology. This allows us to obtain monolayer single crystals with very few defects. However, the size of individual monolayer flakes is generally small. If the yield is low, the procedure cannot easily be scaled up for mass production. New means are therefore being developed to overcome these production barriers.

One of the most promising new technologies devoid of these shortcomings is the separation of thin layers from a bulk crystal using ultrasonic treatment in liquid. This technique can easily be applied to bulk crystals, where interlayer interactions are weaker than intralayer ones. Bulk crystals are dispersed in a solvent, through which ultrasonic waves propagate. The energy of ultrasonic waves causes cavitation inside the bulk crystal, resulting in delamination. However, this technology is also not without drawbacks. The result is a solution containing flakes of different sizes and thicknesses, which can then be separated via centrifugation and fractionation of the solution.

Bulk hexagonal boron nitride (h-BN) has a layered structure similar to graphite that can easily delaminate,

yielding thinner crystals up to a monolayer. Since interlayer interactions in h-BN are weak compared to interlayer covalent bonds, splitting occurs relatively easily. The h-BN (2D) monolayer is stable and has a graphene-like lattice structure composed of alternating boron and nitrogen atoms. The h-BN is an attractive material for barrier layers in heterostructures, since it is one of the strongest known electrical insulating materials with strong prospects for applications in nanoelectronics [2] and optoelectronics [3].

In this work, we obtained thin films of hexagonal boron nitride via the delamination of bulk h-BN crystals by ultrasound. An experimental study of these samples was performed using a variety of optical techniques. Spectra of photoluminescence upon excitation with different energies, reflection and transmission spectra, and dependences of the Stokes parameters of light transmitted through the sample at normal incidence in linear and circular polarizations were studied in particular.

Object of study

Hexagonal boron nitride is a semiconductor with a direct band gap of ~5.9 eV. It is widely used as an insulator for creating 2D heterostructures with ultrahigh mobility that consist of different types of 2D semiconductors (e.g., WSe2 and MoSe2). Single crystal h-BN is an excellent insulator that is characterized by a very high breakdown voltage (>0.4 V nm^{-1}). The hexagonal phase of the layered structure has melting point T > 3000 K at a relatively low density (2250 kg m^{-3}).

Thin films of hexagonal boron nitride were pre- pared on polyethylene terephthalate (PET) substrates. Bulk powder of crystalline h-BN was initially dispersed in a beaker containing a mixture of isopropanol and deionized water in a ratio of 60 : 40. The dispersion was treated using ultrasound with a power of 120 W in an ultrasonic bath (James Products 120 W High Power 2790 mL Ultrasonic Cleaner) filled with deionized water at an initial temperature of 298 K. Five-hour periods of ultrasound treatment were divided into 30 min each to prevent excessive heating of the solvent and ensure a sufficient degree of delamination of bulk crystals. The partially stratified dispersion was then centrifuged for 10 min at 2000 rpm to precipitate residual material and larger particles, narrowing the particle size distribution and favoring thinner particles. Dispersion was fractionated for extracting the supernatant, ensuring that only particles of the suitable size remained. It was then dried in vacuum (0.1 atm, 343 K) on a Schlenk line to completely remove the mixture of solvents. The 606 mg of the resulting powder was then re-dispersed in 12 mL of isopropanol mixed with 8 mL of deionized water to obtain a solution with a certain concentration of ~30 mg mL^{-1}. This redispersed solution was treated with ultrasound for 30 min to ensure uniform dispersion.

To obtain homogeneous thin films from stacked layers of multilayer h-BN, the re-dispersed solution was filtered through a microporous (pores ~0.2 μm in diameter) polytetrafluoroethylene (PTFE) membrane. Films of graphene oxide and molybdenum disulfide obtained in this way have been widely studied, and it has been shown this technology for manufacturing different two-dimensional materials ensures high quality [4–8]. The transfer of thin films obtained by filtering the dispersion was achieved according to the procedure described in [9–11]. The membrane was transferred to the desired substrate while the filtered 2D material was in contact with the substrate. Isopropanol was used to wet the membrane. The substrate was then heated to 70°C. Isopropanol evaporated, releasing h-BN from the membrane. This process can be used with many different substrates. Thin films 1 cm^2 in size were successfully transferred to a substrate for further measurements. The average total thickness of the films formed from individual thin h- BN particles stacked on top of one another was ~5 μm.

Results and discussion

Figure 1 shows a magnified image of the surface of one sample. This snapshot of the surface reveals the sample consisted of thin crystalline h-BN plates with transverse dimensions of up to 5 μm and had 1 to 10 mono-atomic layers. We can see that individual crystals are distributed completely randomly. There are no clearly defined directions on the surface of the sample on either a scale of hundreds of micrometers or a micrometer scale. The Raman spectrum of a thin film showed that the crystal structure corresponds to that of ideal h-BN crystals. At the same time, intense background scattering was observed, indicating a high density of defects in

the film as a whole. Figure 1 shows the sample was opaque, since strong Rayleigh scattering of light was observed on its surface. Rayleigh scattering spectra for linearly polarized light were measured at different angles of incidence ϕ. The spectra had no structure except for one broad maximum with a width of 1 eV at an energy of 1.7 eV. Except for a change in total intensity, there were no qualitative differences between the spectra that depended on angle of incidence ϕ.

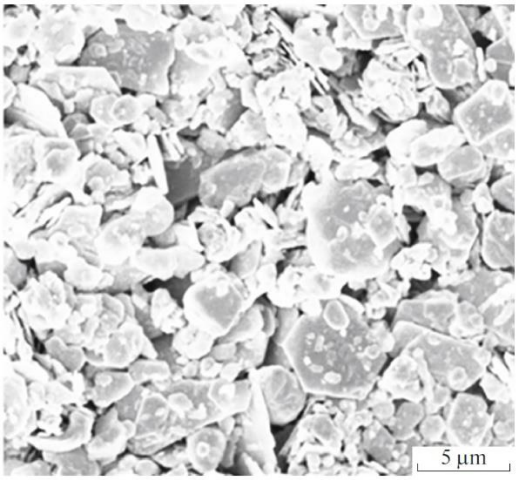

Fig. 1. Images of a sample's surface when magnified by a scanning electron microscope. The scale of magnification is given in the figure.

Spectra of photoluminescence, transmission, and reflection of polarized light from these samples were obtained experimentally. Photoluminescence (PL) spectra were excited with lasers emitting at wavelengths of $\lambda = 244$ nm (5.08 eV), $\lambda = 532$ nm (2.33 eV), and $\lambda = 662$ nm (1.87 eV). A halogen lamp was used to record the transmission and reflection spectra.

A broad PL band ~1 eV wide with a maximum at energy of 3.6 eV was observed in the PL spectra above the indirect edge of the band gap upon excitation with a wavelength of 224 nm. A set of narrow lines in the region of ~1.5 eV was also observed upon excitation at energies below the edge of fundamental absorption of an ideal h-BN crystal (Fig. 2). The emission bands in the depth of the band gap indicate they were associated with deep impurities and color centers. The dependence of the PL spectrum on the energy of the exciting light indicates that intra-center transitions were observed along with band-vacancy transitions. Calculations showed the position of the PL maxima of thin films correlates with the energies of the transition to the energy levels of color centers [12, 13].

Strong absorption with a weakly pronounced structure in the transmission spectra was already observed in the region inside the h-BN band gap at energies above 3 eV. No interference was observed in the 1.3 to 3.0 eV range of transparency, indicating a noticeable change in sample thickness on scales on the order of the light beam's size (~1 mm).

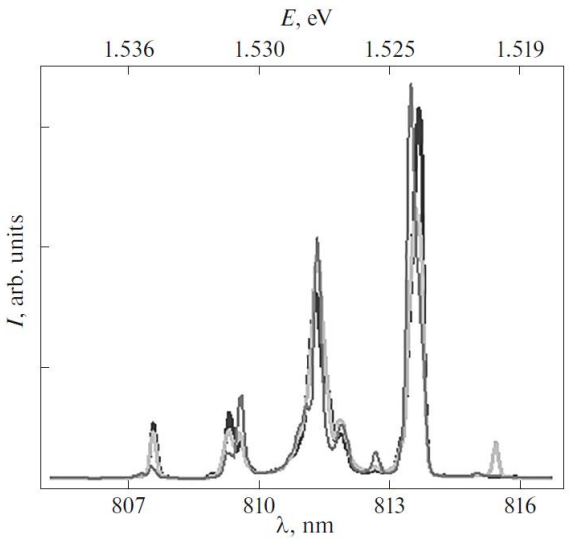

Fig. 2. PL spectrum upon excitation with energy below the fundamental absorption edge of an ideal h-BN crystal (532 nm). T = 300 K.

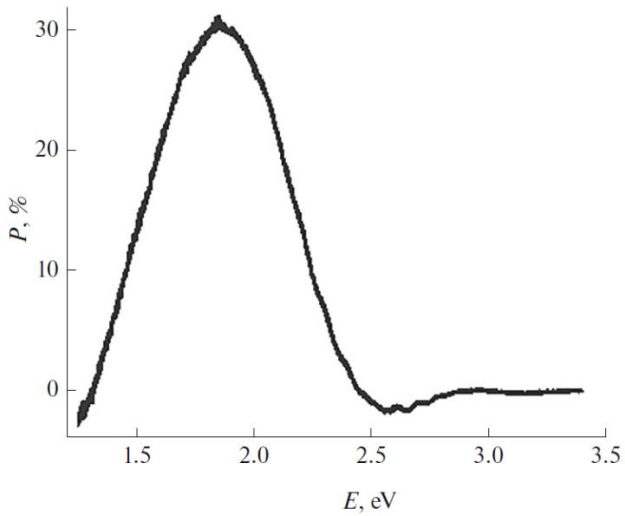

Fig. 3. Spectral dependence of the degree of circular polarization of transmission *P* of the h-BN sample. *T* = 300K.

The transmission spectra of polarized light were measured in the studied samples' region of transparency. The Stokes parameters of the light passing through a sample - the degree of circular polarization (Fig. 3) and the degree of linear polarization - were obtained following the procedure described in [14]. The data show that light birefringence is observed throughout the measured spectral range. When linearly polarized light passes through a sample, it acquires an element of circular polarization (i.e., conversion is observed). The degree of circular polarization changes sign at a wavelength of 550 nm. This is an isotropic point in the spectrum, where the sign of the birefringence changes. At the same time, the effect reaches its maximum at a wavelength of λ ~ 650 nm. Birefringence was measured depending on the point on the sample. It was established that the direction of the optical axis does not change over the entire area of the sample (~1 cm^2).

When splitting bulk h-BN crystals in an ultrasonic bath, the resulting microscopic crystals become electrified as a result of breaking of chemical bonds. During deposition, they stick together in an ordered way, according to the direction of the dipole moment. As a result, their density differs in the distribution of microcrystals. It may not be noticeable to the eye, but it is obvious in polarization. When such dielectric crystals are electrified, electrostatic fields can suffice for ordering.

It has been established that birefringence is a result of the optical axis in a given sample. The emergence of an optical axis in a polycrystalline sample could be due to one of two reasons: the anisotropy of the individual particles themselves or the anisotropy of their collective distribution [15]. Studies with scanning electron microscopy showed the homogeneity of the obtained samples, but studying the Stokes parameters of the light transmitted through a sample allowed us to establish there was latent anisotropy in the optical properties of these films. The co-directionality of the optical axis over the area of a sample was also established, indicating the reason for the anisotropy was not in the properties of individual crystals but in their combined effect on a sample. It was confirmed that the substrate of the considered samples was optically isotropic. Results from changes in the light reflected or scattered from a sample showed that the slope of microcrystals in a thin film is chaotic, in contrast to the case described in [16]. The presence of a hidden order in an unordered structure could indicate we are dealing with a finite system of microcrystals without complete averaging of properties. A similar case of no visible anisotropy but anisotropic light scattering was modeled and analyzed theoretically in [15].

Conclusion

Thin films of hexagonal boron nitride several mono-atomic layers thick were produced by splitting bulk samples in an ultrasonic bath. The transmission, reflection, and photoluminescence spectra of such films were

studied in the region below the edge of fundamental absorption. The spectral dependences of the linear and circular polarizations of light transmitted through a sample were measured. Our SEM study showed no clearly defined directions in a sample. However, birefringence was observed when studying the Stokes parameters of the light transmitted through a sample. It was found the optical axes were co-directional over the area of the sample, while the light scattered by the sample was not polarized. This indicates the reason for the observed anisotropy was not in the properties of individual microcrystals; instead, it is characteristic of each sample and associated with the anisotropy of the filling factor. Statistical analysis of our optical images confirms that thin films exhibit macroscopic ordering of density distributions in the same direction as the optical axis.

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Conflict of interest
The authors declare that they have no conflicts of interest.

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