When the excitation intensity exceeds a threshold (~40 kW/cm²), sharp peaks emerge in the emission spectra. The linewidths of these peaks are ~0.3 nm, which are >50 times smaller than the linewidth of the spontaneous emission peak below the threshold. Above the threshold, the integrated emission intensity increases rapidly with the pump power (Fig. 3B). The narrow linewidth and the rapid increase of emission intensity indicate that stimulated emission takes place in these nanowires. The observed single or multiple sharp peaks represent different lasing modes at wavelengths between 370 and 400 nm. The lasing threshold is quite low in comparison with previously reported values for random lasing (~300 kW/cm²) in disordered particles or thin films (4). These short-wavelength nanowire nanolasers operate at room temperature, and the areal density of these nanolasers readily reaches 1.1x10¹⁰ cm⁻².

The observation of lasing action in these nanowire arrays without any fabricated mirror prompts us to consider these single-crystalline, well-faceted nanowires as natural resonator cavities (Fig. 3C). It is possible that the giant oscillator strength effect (8), which can occur in high-quality nanowire crystals with dimensions larger than the exciton Bohr radius but smaller than the optical wavelength, enables the excitonic stimulated emission in these nanowire arrays. For II-VI semiconductors, the cleaved edge of the specimen is usually used as a mirror (1–3, 17). For our nanowires, one end is the epitaxial interface between the sapphire and ZnO, whereas the other end is the sharp (0001) plane of the ZnO nanocrystals. Both can serve as good laser cavity mirrors, considering that the refractive indices for sapphire, ZnO, and air are 1.8, 2.45, and 1, respectively (18). This natural cavity or waveguide formation in nanowires suggests a simple chemical approach to forming a nanowire laser cavity without cleavage and etching. In fact, when multiple lasing modes were observed for these nanowires (Fig. 3A, inset), the observed mode spacing is ~5 nm for ~5-μm-long wires, which agrees quantitatively well with the calculated spacing between adjacent resonance frequencies $v_r = c/2nl$ (17), where $v_r$ is emission mode spacing, $c$ is the speed of light, $n$ is the refractive index, and $l$ is the resonance cavity length.

Furthermore, lifetime measurements (Fig. 4) show that the radiative recombination of the excitons is a superposition of a fast and a slow process with time constants of ~70 and 350 ps, respectively. The time-resolved spectrum was recorded at an excitation power of 6.39 mW.

18. A simple estimation of the possible number of transversal modes that a waveguide can support indicates that our nanowires with diameters between 80 and 120 nm are actually single-mode waveguides for ultraviolet light.
19. This work was supported by the Camille and Henry Dreyfus Foundation, the J.A. Foundation, the NSF through a Career Award (DMR-0052086), the U.S. Department of Energy, Division of Materials Science of the U.S. Department of Energy under contract DE-AC03-76SF00098. H.K. thanks the Swiss National Science Foundation for financial support. We thank the National Center for Electron Microscopy for the use of their facilities.

2 March 2001; accepted 26 April 2001

FIG. 4. The decay of the luminescence from the ZnO nanowires was studied with a frequency-tripled modelocked Ti:sapphire laser for pulsed excitation (200-fs pulse length) and a streak camera with picosecond resolution for detection. A good fit (solid line) to the experimental data (dotted line) recorded at room temperature is obtained with a biexponential decay model assuming a fast and a slow process with time constants of ~70 and 350 ps, respectively. The time-resolved spectrum was recorded at an excitation power of 6.39 mW.

We report the realization of an ultraviolet light–emitting diode with the use of a diamond pn junction. The pn junction was formed from a boron-doped p-type diamond layer and phosphorus-doped n-type diamond layer grown epitaxially on the [111] surface of single-crystalline diamond. The pn junction exhibited good diode characteristics, and at forward bias of about 20 volts strong ultraviolet light emission at 235 nanometers was observed and was attributed to free exciton recombination.

The wide energy band gap of diamond (5.47 eV) is attractive for the opto-electronic applications because it allows the possibility of ultraviolet (UV) light–emitting devices. Although diamond has an indirect band gap, cathodoluminescence (CL) and photoluminescence (PL) studies have revealed UV luminescence. The UV luminescence is related to exciton recombination from diamond crystals, which have high crystalline perfection. The main luminescence peaks appear at 5.27 eV (235 nm) for free exciton recombination with the assistance of transverse-optical (TO) phonon transition for intrinsic diamond (1, 2), and 5.21 eV (238 nm) (3) and 5.18 eV (239 nm) (4) for bound exciton recombination for doped diamond. The energies of these luminescence peaks are considerably higher than those observed from gallium nitride (GaN) at 3.47 eV (357 nm). Recent studies provided...
convincing evidence of free exciton recombination luminescence from high-quality diamond that can be observed even at room temperature by CL (5) and electroluminescence (6), whereas the other semiconducting materials exhibit the exciton related luminescence only at very low temperatures. This is considered to be due to large binding energy (80 meV) of free exciton in diamond. The result provides the possibility to realize UV light-emitting devices made of diamond.

Concerning the impurity doping of diamond, doping with boron atoms (B doping) leads to p-type semiconducting diamond, which also exists in nature and can be reproducibly obtained by either chemical vapor deposition (CVD) or high-pressure growth techniques. Although n-type diamond does not exist in nature, thin films of n-type diamond have been grown by a CVD process with phosphorus (P) doping (7). We successfully grew both B- and P-doped diamond thin films on Si surfaces of diamond with high crystalline perfection. Here we report the formation of a pn junction diode along with the optical emission characteristics of the diode.

Each B- and P-doped diamond thin film was independently grown with the use of individual microwave plasma enhanced CVD systems. Metal chamber-type CVD systems with the background pressure of 1 × 10⁻⁸ torr were used to avoid incorporation of unexpected impurity such as silicon and nitrogen [see (8) for a detailed description]. Mechanically polished [111] surface of B-doped single crystalline diamond with the resistivity of around 10⁻² Ωcm was used as a substrate. The size of the substrate is 2 mm² with a 0.5-mm thickness. The steps of the formation process of pn structure are as follows: (i) cleaning of substrate surface, (ii) growing of B-doped layer, (iii) cleaning of the sample, (iv) growing of P-doped layer, (v) cleaning of the sample, and (vi) forming of ohmic electrodes for both the layers. For steps (i), (iii), and (v), a chemical oxidation process was applied using an acid mixture of HClO₄, H₂SO₄, and HNO₃ at a ratio of 1 : 3 : 4 and a temperature of 200°C for 30 min, resulting in the removal of nondiamond adsorbents from the sample surface and the termination of the surface with oxygen in place of hydrogen. Each B-doped and the P-doped layer was grown using trimethylboron [(TMB), (CH₃)₃B] and phosphine (PH₃), respectively, as impurity source gases (9, 10). The electrical properties of each layer have been characterized by Hall measurements using the layers grown simultaneously on separate insulating diamond substrates, with p-type and n-type conductivity confirmed for B-doped and P-doped layers and showing a carrier activation energy of 0.37 and 0.59 eV, respectively. These values are in good agreement with the published data for those impurity-doped diamonds (8, 11). The carrier mobility of the B-doped and the P-doped layer is 300 cm²/V·sec and 60 cm²/V·sec, respectively, at room temperature. Lastly, the ohmic electrodes were formed for both the p-type and n-type layers. For the p-type layer, we deposited a Ti film (thickness 100 nm) with an Au evaporated film (also 100 nm thick) for protection. The films were deposited at 400°C to make a better ohmic interface. For the n-type layer, Au ion implantation was performed (12, 13) through a mask to make graphitic dots with a depth of 30 nm and a diameter of 150 μm at 20 to 25 different points on the surface. The acceleration voltage and the dose were 40 keV and 10¹⁶ cm⁻², respectively. The implanted dots were covered by Ti and capped with Au film for protection. The sample was annealed in high vacuum (5 × 10⁻⁶ torr) at 850°C for 1 hour to ensure the stability of the implanted contacts during diode operation. The annealing process does not affect the electrical properties of the p-type and n-type layers. Also, at such annealing temperature we do not expect appreciable inter-diffusion of impurities through the pn junction. To check the impurity concentrations of each layer and interdiffusion, secondary ion mass spectrometry (SIMS) analysis was performed for the pn structure grown on insulating diamond substrate at the same growth condition (Fig. 1).

The impurity concentrations of B-doped and P-doped layers are 1 to 2 × 10¹⁷ cm⁻³ and 7 to 8 × 10¹⁸ cm⁻³ and thicknesses of about 1 and 2 μm, respectively. The doping profile is almost uniform for each P- and B-doped layer, and there is no intermixing region at the pn interface.

Current–voltage (I–V) characteristics of the pn junction show clear rectifying property (Fig. 2A). The rectification ratio was about three orders of magnitude when forward (n-type negative) and reverse (n-type positive) voltage applied at ±15 V (Fig. 2B). The reverse current is rather high (about 10⁻³ A at −20 V) due to the imperfection of the junction at specific portions of the sample. Due to the large reverse current, the turn-on voltage (6 to 7 V) is observed at a higher than expected value (4 to 5 V). A strong deviation of the I–V profile from the exponential relation over an applied voltage of 10 V is due to high series resistance of the sample (mainly of the P-doped layer) of more than 10⁶ ohms. When the forward current exceeds 10⁻⁴ A, the temperature of the sample rises by spontaneous resistive heating, and, as a result, the I–V profile becomes steeper. The capacitance–voltage characteristic shows an increase of capacitance according to the
increase of the voltage in a reverse voltage region, confirming the existence of a depletion layer and its narrowing according to the voltage increase.

For forward currents exceeding 0.1 mA, light emission was observed. In the present structure of the samples, light emission was observed around the electrode of the sample because the pn junction and the light-emitting area exist behind the electrode and because the driving voltage is applied perpendicular to the sample surface (Fig. 3 inset). As we increased the forward current, we observed the UV light emission in the spectrum (Fig. 3). The driving voltage is applied perpendicular to the sample surface (Fig. 3 inset). As we increased the forward current, we observed the UV light emission in the spectrum (Fig. 3). The driving voltage in a reverse voltage region, confirming the existence of a depletion layer and its narrowing according to the voltage increase.

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Several (amino)(aryl)carbenes have been shown to be stable at room temperature in solution and in the solid state. Electroneutrality of the carbene center is ensured by the amino group, which has both π-donor and σ-acceptor electronic character. The aryl group remains a spectator substituent, as shown by single-crystal X-ray analysis and by its chemical behavior. Because only one electron-active substituent is needed, numerous stable carbenes will become accessible, which will open the way for new synthetic developments and applications in various fields.