High carrier mobility on hydrogen terminated (100) diamond surfaces

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An increase in carrier mobility from typical values around 100 to more than 300 cm²/V s at room temperature is detected on hydrogenated undoped (100) diamond layers after annealing at 400 K in a vacuum. As a function of temperature in the range 400 to 125 K the high mobility followed tendencies remarkably close ionized impurity (toward low temperatures) and phonon scattering (toward high temperatures). As a function of annealing time, the high mobility increased with the time constant of about 6.8 h in the range of 1–16 h. A prerequisite for obtaining the largest increase in mobility was optimized surface cleanliness. Exposing the samples to air resulted in a complete recovery of the original values of mobility, hole concentration, and conductivity after several days. The data are discussed in terms of interactions between holes in the surface conductive channel and adsorbates on the surface. © 2006 American Institute of Physics.

Surface conductivity of hydrogen-terminated diamond attracts a lot of attention as a unique phenomenon and therefore interesting from the viewpoints of basic physics as well as applications. The electronic properties of diamond conducting surfaces are commonly studied by Hall effect experiments which reveal hole type conduction with mobility between 1 and 100 cm²/V s and sheet hole density in the range of 10¹⁰–10¹³ 1/cm². Generally, a decrease in mobility with increasing carrier density is detected, but a clear description of this phenomenon and affecting parameters is still missing.

Theoretical calculations indicate that the conducting layer is only a few nanometers thin and thus two-dimensional (2D) properties should dominate. Up until now, however, no experimental evidence for 2D transport has been reported. This may be due to effects of surface roughness, grain boundaries, and defects at the surface. In particular because most of the Hall experiments were performed on polycrystalline chemical vapor deposition (CVD) diamond with undefined surface morphologies. In addition, ionized molecules in the surface adsorbate layer, which are required for surface conductivity, may act as scattering centers for holes. Due to the desorption of adsorbates, the surface conductivity is generally observed to decrease as a function of annealing temperature and duration. But only little data on mobility and carrier density are available in the literature taking into account effects of annealing at elevated temperatures.

In this letter, we report about hole mobilities and sheet hole densities measured on intrinsic (100) oriented single-crystalline CVD diamond with an atomically flat surface. The hydrogen-terminated surface is exposed to air, giving rise to the formation of an adsorbate layer, and then characterized by Hall effect measurements. To reveal scattering mechanisms, temperature dependent experiments are performed after annealing steps at elevated temperatures to partially desorb the adsorbate layer.

Undoped homoepitaxial diamond layers of 1 μm thickness were deposited on synthetic (100) Ib diamond substrates (3 × 3 mm size) by microwave plasma CVD with the following parameters: Sample temperature 800 °C, power 750 W, gas pressure 25 Torr, hydrogen flow 398 sccm, and methane flow 2 sccm. The deposition under these conditions results in an atomically smooth surface of high electronic quality.

The diamond surface was cleaned by organic solvents (acetone, isopropanol, water) and by mechanical cleaning in order to achieve a well-defined interface between the diamond and surface adsorbates. The samples were characterized by Hall effect measurements using 4 mm contacts of 0.3 mm diameter were evaporated at the sample corners, which resulted in 2 mm contact distance. The Hall measurements were performed in ambient air at 300 K and then at low pressure (≈1 Torr) in argon as a function of temperature. Prior to the temperature profiles, the samples were annealed at 400 K for a given period of time.

Typical Hall mobilities and sheet hole concentrations in air and as a function of temperature after 1 h annealing in vacuum are plotted in Fig. 1. At room temperature, the mobility increased after 1 h annealing from original 114 cm²/V s to about 223 cm²/V s. The sheet carrier concentration was strongly affected by thermal annealing: It decreased from 7 × 10¹² cm⁻² to 6 × 10¹¹ cm⁻². The sheet conductivity decreased from 1 × 10⁻⁴(Ω/sq)⁻¹ to 2 × 10⁻⁵(Ω/sq)⁻¹. Obviously, the increasing carrier mobility is accompanied by decrease in carrier concentration and rise of resistivity.

As a function of temperature, the mobility shows a monotonic increase toward high temperatures over the whole temperature range, with an activation energy of 9–23 meV. This is in good agreement with previously reported data which showed that transport properties of holes at hydrogenated diamond surfaces are near to metallic.

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The time evolution of the mobility and sheet carrier concentration at the annealing temperature of 400 K is shown in Fig. 2(a). During annealing, the carrier concentration decays exponentially $\approx \exp(-t/\tau)$ (white curve) with a time constant of $(6.8\pm0.3)\text{h}$. At the same time, the mobility increases, which is well fitted by an exponential increase of $\mu \approx (1 - \exp(-t/\tau))$ (black curve) using the same time constant.

Figure 2(b) displays the mobilities and carrier concentrations measured at 300 K after annealing at 400 K for 1 to 16 h. Compared to the data at 400 K [Fig. 2(a)], a more pronounced increase of mobility (open symbols) with annealing time is detected with values reaching up to $328 \text{cm}^2/\text{V}\cdot\text{s}$ after 16 h. The sheet carrier concentration (full symbols) decays in correlation with the mobility.

Exposing the samples to air for several days results in a complete recovery of the original values of mobility, hole concentration, and conductivity. The recovery indicates that the annealing did not degrade the diamond surface H termination but rather modified the properties of the adsorbate layer on the diamond surface.

The most pronounced increase in mobility was enabled by mechanical cleaning step on hydrogenated surfaces. Prior to cleaning the mobility of holes at room temperature was $92 \text{cm}^2/\text{V}\cdot\text{s}$ in air and increased to $115 \text{cm}^2/\text{V}\cdot\text{s}$ after 1 h annealing in vacuum. Using mechanical cleaning, the mobility was typically $114 \text{cm}^2/\text{V}\cdot\text{s}$ in air and increased further to $223 \text{cm}^2/\text{V}\cdot\text{s}$ after 1 h annealing in vacuum. The sheet carrier concentration decreased after cleaning by about a factor of 1.5. Further research is required to elucidate details of this phenomenon. For instance, recent report indicates that a carbon deposit may be generated during a plasma hydrogenation process and its removal by mechanical treatment improves hydrogen related properties of diamond surfaces.

As illustrated in Fig. 1, the mobility decreases toward lower or higher temperatures from a maximum centered at 250 K. The decrease is remarkably close to the tendencies corresponding to ionized impurity scattering $\approx T^{-3/2}$ toward lower temperatures and phonon scattering $\approx T^{-3/2}$ toward higher temperatures. These power-law tendencies were introduced for bulk three-dimensional scattering processes. Yet, even in 2D systems the carrier transport is dominated by three-dimensional effects if carrier mobilities are relatively low ($<1000 \text{cm}^2/\text{V}\cdot\text{s}$).

Considering the transfer doping model of hydrogenated diamond, the exponential decay of carrier concentration with annealing time indicates thermal desorption of surface adsorbates. Since the time constant of the desorption process is expressed as $\tau=(1/\nu_0)\exp(E_d/kT)$ the desorption energy can be calculated by:

$$E_d = kT \ln(\tau \nu_0).$$

(1)

Using $\tau=6.8 \text{h}$ and typical attempt-to-escape frequency prefactor $\nu_0 = 10^{13} \text{s}^{-1}$, Eq. (1) yields $E_d = 1.10 \text{eV}$. The calculated desorption energy is higher than 0.5 eV typical for physisorbed water molecules. The additional energy may arise from the fact that the decrease of hole concentration in the surface channel requires not only desorption but also transfer of electrons from adsorbate layer back into diamond via an electrochemical reaction.

Based on our data, we assume that due to the small separation (few nanometers) between holes in the surface conductive channel and ions in the adsorbate layer on the surface, holes are scattered by electrostatic interaction with ions. Thus, the annealing leads to higher mobilities by reducing the concentration of ionized adsorbates at the surface.

Surface conductivity of diamond is established by equilibration of the chemical potential in the surface adsorbate layer and the Fermi level in diamond via tunneling of electrons from the diamond valence band into the adsorbate layer which acts as an electrolyte. Solvation of particular gas molecules ($\text{H}_2$, $\text{O}_2$, or $\text{CO}_2$) in the adsorbate layer is required to establish the transfer reaction. At elevated temperatures, the chemical potential in the adsorbate layer de-
creases (moves upward) based on the Nernst equation
\[ \mu (H_2/H^+) = -4.44 + kT \log H \].
This is illustrated by Fig. 3 which shows theoretical calculation of chemical potentials in electrolytes with pH ranging from 2 to 6 as a function of temperature. In addition, at elevated temperatures the solubilities of gas molecules, which are essential for surface conductivity (e.g., H_2, O_2, CO_2), decrease and the molecules desorb from the adsorbate layer. The gas desorption results in an increase of the pH of the adsorbate layer, which contributes to the lowering of the chemical potential. Due to the decrease of chemical potential, electrons are transferred from the electrolyte back into diamond giving rise to a decrease in the density of chemical potential, electrons are transferred from the electrolyte back into diamond giving rise to a decrease in the density of chemical potential, electrons are transferred from the electrolyte back into diamond giving rise to a decrease in the density of chemical potential.

The model so far implies that the mobility should decrease and carrier density increase again if the temperature is decreased back to room temperature. This is indeed observed when the film is exposed to air, where the thermally desorbed adsorbate layer is replenished with new adsorbates and gas contamination. If the sample remains in a vacuum, the adsorbate layer does not recover. Thus, all detected variations of hole mobility can be attributed to a change in adsorbate layer quality. Schematic drawing of the model is presented in Fig. 4.

To conclude, the mobility of holes at room temperature in undoped hydrogen terminated diamond layers significantly increased from typical values around 100 cm^2/V s on as-hydrogenated surfaces to more than 300 cm^2/V s after vacuum annealing. This increase is attributed to a desorption of adsorbates and solvated gas molecules out of the surface adsorbate layer. This results in an upward shift of the chemical potential in the adsorbate layer and hereby in a change of the electrochemical equilibrium between the diamond and adsorbate layer, which affects the accumulation of holes in the surface conductive channel. Consequently, the concentration of holes decreases and the mobility increases, because of the reduced concentration of ions at the diamond/adsorbate layer interface.

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