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Spintronics and thermoelectrics in exfoliated and epitaxial graphene
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Appendix: experimental methods

There are a number of techniques that are required for the fabrication and measurements of the nanodevices that where studied in this thesis. In the appendix, I explain the general concepts of these techniques. The recipes that we used for individual devices are described in the main text.

Device fabrication

Nanodevices are typically fabricated by lithography, which is the creation of small-scaled patterns of various materials on a substrate. This is done by spin coating the substrate with a thin, sacrificial polymer film, called the resist. The polymer is then patterned by exposing some parts of the film to light or to an electron source, which breaks down the polymer chains and thus changes its chemical properties. This modification allows for selectively removing the desired parts of the polymer film with the right solvent, a step called development. The developed polymer pattern on the sample now allows for some flexibility: either the uncovered pattern is removed by etching, or a desired material is deposited. In the last step the remaining polymer layer is removed, leaving on the substrate the designed pattern of the material of interest. Doing several of these steps after each other allows for making the kind of devices used throughout the experimental part of this thesis.

Deep-UV photolithography   In photolithography, light is used for the exposure of the polymer. Patterning is done using a pre-designed shadow mask that partially blocks the lamp used for exposure, thus creating a pattern. The resolution of this method depends on the wavelength of the light. When the smallest features of the pattern reach the size of the wavelength, interference effects start to play a role. This may lead to blurred features, such as rounded edges of the pattern. Also the distance between the mask and the resist plays a role: pressing the mask on the resist layer

(hard contact) increases the resolution. Deep UV light (we use 240-350 nm) has a good resolution of down to a micrometer.

A general problem in lithography is that the deposition of a thin metal layer on the resist can be hard to remove, because the layer covers the whole sample in a continuous film. Thus, the solvents used for removal of the polymer are blocked by the metal layer on top. A solution to this problem is the creation of an undercut: a slight overhang of the sidewalls of the resist layer at the pattern edges. This causes the metal film to be discontinuous at these edges, allowing the solvents to remove the polymer and assuring a good lift-off of the resist layer after metal deposition. To achieve a good undercut, a double resist layer can be used. In the works presented in this thesis, we use the photo-resist ZEP-520A (ZEON Corporation) and develop by n-amyl acetate, after which we use the lift-off resist LOR-3A (MicroChem), which can be removed by a mixture of 1:1 isopropyl alcohol (IPA) and de-ionized (DI) water. Thus, the undercut is ensured, because the lift-off resist is removed through, and slightly underneath, the developed photo-resist. This allows for easy removal of the polymer by a resist stripper like Remover PG (MicroChem), even after the deposition of a metal film.

Electron beam lithography   Electron beam lithography (EBL) uses a focused electron beam for the lithographic exposure step. EBL has a very high resolution, up to several tens of nanometers, so it is ideal to pattern the smallest features of the nanodevice. This method uses a dedicated design for each individual device. Because of this, and because each pattern is written line-by-line, it is more time-consuming than photo-lithography. Patterning software like E-line from Raith makes it possible to save some time by the use of an automatic alignment procedure for multiple exposures of several devices in a row.

The pattern resolution and quality are determined by a number of factors, including the electron energy, the total dose, the resist composition and thickness. As EBL-resist, usually a single layer of poly(methyl methacrylate) (PMMA) is used. EBL allows for the creation of an undercut, even with a single layer resist, by exposing with low energy electrons (low acceleration voltage). Low energy electrons undergo stronger forward scattering when entering the resist layer, resulting in a broadening of the beam towards the sample. High acceleration voltage results in a pattern with straight edges. The PMMA is developed in a mixture of 1:3 methyl isobutyl ketone (MIBK) and IPA. It is also possible to use a negative resist, such Ma-N 2410 (MicroChem). In this case, development does not remove the exposed pattern, but the unexposed parts (the negative of the pattern). This procedure is used for removing large parts of the sample or for covering most of it with a deposition material.

During EBL exposure, it is essential that there is a pathway for the electrons to dissipate to the ground. Otherwise the substrate charges, thereby repelling the electron beam and leading to loss of resolution and alignment. This can be done by using a conductive polymer like aquaSAVE (Mitsubishi Rayon), which is spin coated

before exposure and removed with DI water before development.

Reactive ion etching   Removing materials like graphene can be done by placing it in a radio-frequency (RF) plasma chamber. This procedure is called reactive ion etching (RIE). The plasma is created by applying an ac voltage on a gas, exciting the electrons to leave the gas atoms and form a plasma. For the removal of graphene we use an O_2 plasma. The high kinetic energy of the O_2 ions knocks out the surface atoms of the exposed graphene, while the parts protected by a polymer layer are unaffected. The etch rate can be precisely tuned, even below nm s^{-1}, using the RF power applied to the plasma.

Electron beam evaporation   A common method for the creations of thin films is by electron beam evaporation. A socket with the required material is placed in a in high vacuum chamber in the order of 10^{-6} mbar or below. An electron beam is focused on the target using a magnetic field. This heats up the material, which will cause the atoms to leave the target and travel in a straight line towards the sample. The deposition rate can be fine-tuned, also below a nm s^{-1}, by changing the intensity of the electron beam. Electron beam evaporation is used to deposit non-magnetic and magnetic metals. It also possible to deposit oxides, usually with the help of an oxygen back pressure in the chamber to achieve a more uniform film with less oxygen vacancies and other defects.

Electronic characterization

Measurement setup   For the electronic measurements of the nanodevices in this thesis, we glued the chip containing the sample with some silver paint to a chip carrier and connected the wires of the devices with the pins of the carrier using a wire bonder. The sample was then loaded in a vacuum chamber (pressure below 10^{-6} mbar), where it was connected to the measurement setup. In our setup, Helmholtz coils are used to apply magnetic fields of up to 1 T. A liquid helium (He) flow cryostat is used to cool down the samples down to very low temperatures. In such a system, liquid He (nitrogen can also be used) is continuously pumped through a channel separate from the sample, but in close thermal contact. By actively controlling the pressure and the flux of the He it is possible to even cool down below 4.2 K, the boiling point of He at ambient pressure. Temperatures between $\sim$ 4 K and room temperature are obtained using a heater and a temperature control loop. The heater can also be used to warm up the sample above room temperature.

Electronic characterization typically is done by sending a known current *I* through the device and measuring its voltage response *V* (IV-characterization) in one of the configurations described throughout the thesis. Alternatively, it is possible to measure the current response to an applied voltage (VI). VI measurements are useful to

test capacitive elements of the circuit (such as a back gate), because a sufficiently low voltage doesn't force a current through the circuit if there are no current paths available, thus avoiding a breakdown of the circuit. For most measurement presented in this thesis however, we use IV measurements. For this, we use a voltage source, which is connected to the device via a custom build IV measurement box that converts this voltage into a current and amplifies the signal. Between the sample and setup there are low-pass filters to reduce high frequency noise and voltage peaks from outside sources. The voltage source can be a general purpose device (such as the Keithly 2410) or a lock-in amplifier (Stanford Research Systems SR844). The lock-in technique provides several advantages, which will be described in more detail in the next paragraph.

All voltage and current sources and controllers, including the current source powering the magnet, are connected via a GPIB connector (this stands for General Purpose Interface Bus, an 8-bit digital communication channel) to a pc with dedicated LabView software to control all the system inputs and record the measured voltage output.

Lock-in amplifier   A lock-in amplifier is an electronic measurement device that can be used to filter out environmental noise many times higher than the signal of interest. In our measurement setup we use it to generate the input voltage (which can be converted to a current by the IV-measurement box) and also measure the system response. Another advantage is the easy measurement of higher harmonic responses to the applied electronic signal.

In the lock-in amplifier scheme, a time-varying carrier signal is generated by modulating a static excitation under the condition that the time variation is quasi-static, meaning slow enough for the system to instantaneously equilibrate itself (most measurements in this thesis are done in the frequency regime below 20 Hz). This modulated input voltage is given by $V_i \sin(\omega_i + \theta_i)$, with amplitude V_i, frequency ω_i and phase θ_i. The low noise output signal is obtained by multiplying it with a reference signal with the same frequency, and then averaging out this result by integrating over time (typically, the integration time is $3/\omega_i$ or higher).

The reference signal $V_{\mathrm{ref}} \sin(\omega_{\mathrm{ref}} + \theta_{\mathrm{ref}})$ can be produced by the internal reference of the lock-in amplifier. The output voltage is given by the product:

$$
\begin{aligned}
V_{\mathrm{out}} &= V_i V_{\mathrm{ref}} \sin(\omega_i t + \theta_i) \sin(\omega_{\mathrm{ref}} t + \theta_{\mathrm{ref}}) \\
&= \frac{1}{2} V_i V_{\mathrm{ref}} \cos((\omega_i - \omega_{\mathrm{ref}})t + \theta_i - \theta_{\mathrm{ref}}) + \frac{1}{2} V_i V_{\mathrm{ref}} \cos((\omega_i + \omega_{\mathrm{ref}})t + \theta_i + \theta_{\mathrm{ref}})
\end{aligned}
$$

$$(10.5)$$

This signal consists of two terms. The second term is a time-varying signal with high frequency. The frequency of the first term is proportional to frequency difference between input and reference signal. If the system is excited at the reference frequency

$(\omega_i = \omega_{\text{ref}})$, the first term becomes a time invariant signal given by:

$$V_{\text{out}} = \frac{1}{2}V_i V_l \cos(\theta_i - \theta_{\text{ref}}) \tag{10.6}$$

This signal can be separated from all time-varying signals using a low pass filter with a sufficiently narrow band. The power of the lock-in lies in the fact that a low-pass filter can have a bandwidth that is much narrower than a bandpass filter around ω_i. The term lock-in comes from the necessary requirement of phase-locking, that is, $\theta = \theta_i - \theta_{\text{ref}}$ cannot vary over time in order for V_{out} to stay a static signal.

A two phase lock-in uses a second reference signal subjected to a 90° phase-shift, which overcomes the fact that $V_{\text{out}} = 0$ when $\theta = 90°$. Thus, it is possible to measure the full amplitude of the signal by employing $V_{\text{out}} = R = \sqrt{X^2 + Y^2}$, with $X = V_{\text{out}} \cos\theta$ and $Y = V_{\text{out}} \sin\theta$. The two phase lock-in amplifier is necessary for nonlocal measurements, because nonlocal signals typically have a phase shift of $\theta = 90°$.

The lock-in allows for the measurement for higher harmonic responses to a dynamic excitation of the system. This is because the output voltage can be written as the following expansion:

$$V_{\text{out}} = IR_1 + I^2 R_2 + I^3 R_3 + \dots \tag{10.7}$$

By setting the reference signal to a frequency with n times the excitation frequency, we obtain the contributions depending on I^n. The voltage responses up to the third order (i.e. for $n = 1, 2, 3$) are given by:

$$\begin{aligned}
V_1 &= R_1 I_0 + 3/2 R_3 I_0^3. \quad \theta = 0° \\
V_2 &= 1/\sqrt{2} I_0^2 R_2, \quad \theta = -90° \\
V_3 &= -1/2 I_0^3 R_3, \quad \theta = 0°
\end{aligned} \tag{10.8}$$

Thus, it is possible to determine higher order contributions to the measured voltage signal. In chapter 10 we make use of this feature of the lock-in for measuring Joule heating, where the response is of the second order ($\propto I^2$) and can thus be distinguished from the linear ($\propto I$) Peltier effect.