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ETCHING EFFECTS OF LOW TEMPERATURE HYDROGEN PLASMA ON ENCAPSULATED DIAMOND TRANSISTORS

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We study etching effects of low temperature hydrogen plasma treatment (200–300 °C) in two different microwave plasma reactors (linear and focused plasma) on diamond solution-gated field-effect transistors with various polymers for encapsulation (MA-P, OFPR, SU8). Three-dimensional transistor microstructures (20 μm) are grown from nanocrystalline H-terminated intrinsic diamond by MW-CVD on Si/SiO_2 substrates. We observe increased etching rates of the polymers in dependence on temperature of hydrogenation (from 3 to 400 nm/min). We show that low temperature hydrogenation in linear plasma system is due to larger distance (7 cm) between the high-density plasma region and the sample surface less aggressive on encapsulation and 3D transistors based on surface conductivity of H-terminated diamond are fully operational after this treatment.

1. Introduction

Diamond exhibits unique combination of electrical, optical and mechanical properties with chemical and biocompatible properties [*Tang et al.*, 1995, *Kalbacova et al.*, 2007] and it is a perspective material for bioelectronic and electrochemical applications. Diamond films can be employed as biosensors such as capacitive sensors [*Abouzar et al.*, 2008] or solution-gated field-effect transistors (SGFETs) [*Rezek et al.*, 2010, *Dankerl et al.*, 2009]. These biosensors are often encapsulated by different

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types of photoresists which are relatively easy to prepare and remove. Silicon nitride can represent other way of encapsulation [*Sakata et al.*, 2004] but its preparation is more complicated.

Common diamond field-effect transistors with gate immersed in solution based on hydrogen terminated diamond surface conductivity are prepared by diverse technological steps including lithography, lift-off, selective oxidation, encapsulation, deposition of contacts etc. [*Rezek et al.*, 2010, *Krátká et al.*, 2012]. This is complicated for renewal of device because standard recycling process includes cleaning in piranha solution, acid boiling, using aqua regia for removing gold contacts, oxygen plasma treatment etc. This process destroys C–H surface termination. Therefore, H-terminated diamond SGFETs must be prepared from the beginning after the sensor has been used because for instance adsorption of proteins causes permanent shift of the characteristics in spite of rinsing [*Rezek et al.*, 2010]. A direct growth of diamond structures via patterning of nucleation/seeding layer can represent an alternative solution [*Kromka et al.*, 2009, *Kozak et al.*, 2010, *Babchenko et al.*, 2012].

Therefore, we employ here nanocrystalline diamond (NCD) films to fabricate directly grown SGFET microchannels. We study if such complete encapsulated devices can be recycled by low temperature hydrogenation (LTH) process in order to clean and at the same time preserve active area of H-terminated diamond surface. Moreover, we study effects of low temperature hydrogen plasma treatment (200–300 °C) in two different microwave plasma reactors (linear and focused plasma) on diamond transistor characteristics and on etching of organic resins encapsulation.

2. Experimental methods

Directly grown NCD FET channels were prepared by initial patterning of diamond nanoparticle nucleation film on Si/SiO_2 substrates using photolithographic processing with two polymer layers and by subsequent reactive ion etching through photolithographic mask [*Babchenko et al.*, 2010]. Afterwards, growth of NCD microstructures was performed in a microwave plasma CVD system (AIXTRON P6) from a methane/hydrogen gas mixture. Process parameters were as follows: microwave power 2.5 kW, 1 % methane in hydrogen, total gas pressure 50 mbar, substrate temperature 800 °C, and total growth time 3 h [*Babchenko et al.*, 2010]. The surfaces of diamond structures were hydrogenated in pure H plasma at 600 °C for 10 min.

Source and drain contacts were prepared by thermal evaporation (10 nm of Ti and 50 nm of Au) followed by lift-off technique. The area between contacts was covered with positive photoresist OFPR (thickness 2.5–4 μm) or ma40 (thickness 3–4 μm) or with negative photoresist SU8 (thickness 10 μm) and deep UV curing of the resists for hardening and biocompatibility was applied. An opening of $60 \times 60\ \mu m^2$ in resist was made in the active area of the device [*Rezek et al.*, 2010]. Thickness of the polymer encapsulation was measured by profilometer before and after each LTH experiment. Polymer etching rates were calculated from the thickness difference and process time.

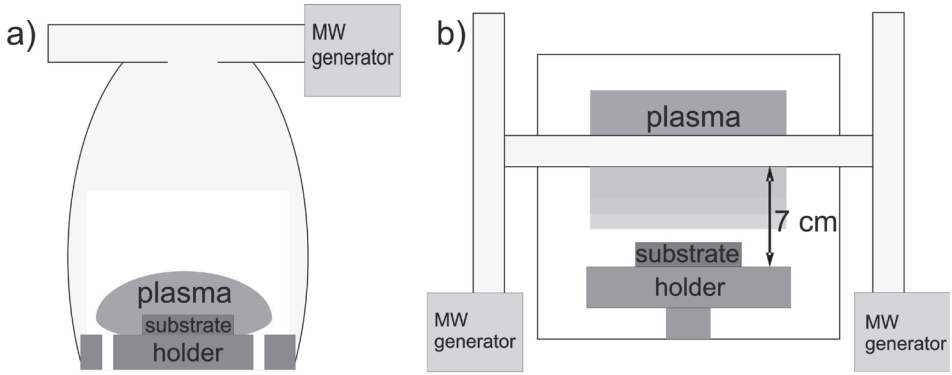

FIGURE 1. Diamond microwave CVD reactors: (a) focused plasma reactor, (b) linear antenna reactor.

Commonly used relatively high substrate temperatures ($T \geq 600\,^{\circ}\mathrm{C}$) during diamond growth and hydrogenation can lead to partial or complete damage of the metal electrodes or other electronic parts [*Neykova et al.*, 2009]. Thus, 3D transistors including the encapsulation and gold contacts were exposed to hydrogen plasma using low temperature in two microwave plasma reactors (focused plasma reactor and linear plasma reactor). Figure 1 shows schematic drawing of the two fundamentally different setups and conditions of focused and linear antenna MW plasma reactors. The parameters of LTH in focused plasma were as follows: microwave power 800–1500 W, vacuum pressure 20–30 mbar, hydrogen flow 300 sccm, temperature 300 °C (the lowest achievable), processing time 20 min. As for LTH in linear plasma, the parameters were as follows: microwave power 1000 W, vacuum pressure 0.3 mbar, hydrogen flow 100 sccm, processing time 20 min. Temperature was varied in the range of 200 °C and 300 °C with the accuracy of ±10 °C.

3. Results and discussion

Figure 2 shows different etching rates for different types of encapsulation after LTH process. The etching rates of each encapsulation material increase (from 3 to 400 nm/min) in dependence on temperature of hydrogenation (200 °C–300 °C). Error bars of ±10 °C along the X axis show the inaccuracy of the temperature measurement during the process. All data are related to linear plasma except for SU8 3010 at 300 °C ("star") which has been obtained after focused plasma LTH. This etching rate is bottom estimate because all employed photoresists were completely removed in focused plasma at 300 °C which you can see in optical images of active area of the transistors (Figure 3). As for gold contacts, their quality appears good even after LTH in focused plasma.

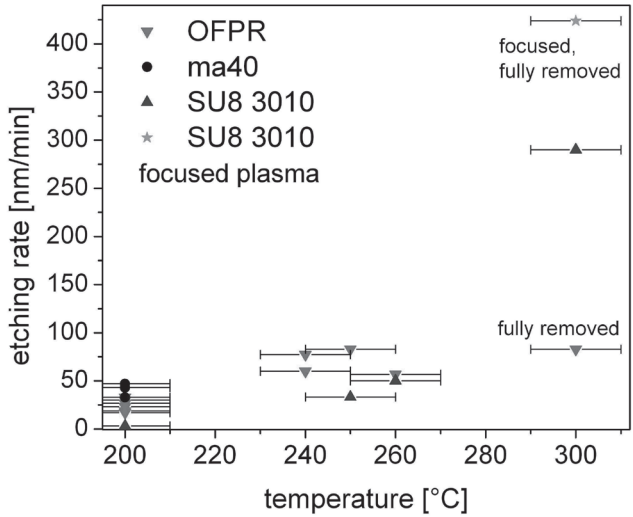

FIGURE 2. Etching rates for photoresists (OFPR, ma40 and SU8 3010) as a function of temperature.

LTH in linear plasma is less aggressive on encapsulation than focused plasma most likely due to larger distance between the high density plasma region and the sample surface [*Kromka et al.*, 2012, *Neykova et al.*, 2012]. Based on the data of LTH in linear plasma, photoresist SU8 is the most stable of employed photoresists and it can be used up to 300 °C. Photoresist OFPR is removed during LTH process in linear plasma at temperature about 260 °C and its quality is good up to this temperature. Photoresist ma40 appears as the least stable, having bad quality (cracks and bubbles) already at 200 °C.

Figure 4 shows that channel currents after LTH are reduced compared to the current after standard hydrogenation at 600 °C in focused plasma. Yet 3D diamond transistors are fully operational after LTH at 200 °C in linear plasma reactor even after repeated LTH process. This is in agreement with the study of hydrogen termination at 200 °C performed in linear antenna plasma system which is efficient to induce hydrogen-terminated conductive surfaces and an increase in substrate temperature up to 400 °C results in an increase in surface conductivity [*Neykova et al.*, 2012]. When LTH was repeated on the same device we observed fluctuations of threshold voltage Ut within about 150 mV. Transconductances (slope of $I_{ds}(U_g)$) calculated at I_{ds} in the linear region of transfer characteristics are 10.6 nS, 12.9 nS and 12.2 nS at $U_{ds} = -0.6$ V, $I_{ds} = -2.0$ nA for transfer characteristics after first, second and third LTH process, respectively. Thus transconductance remained similar. This indicates that the fluctuations are related to the variation of gate potential but not to the equilibrium of surface conductive layer. This is unlike the case when proteins were adsorbed on the surface [*Rezek et al.*, 2010]. On the other hand, it is in a good agreement with

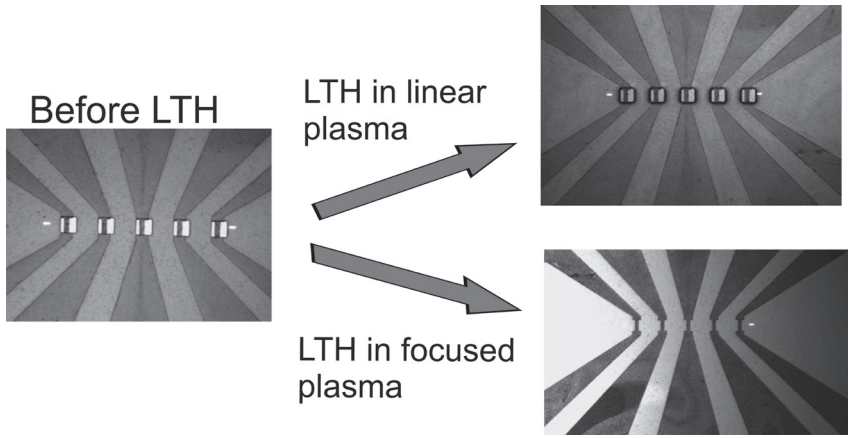

FIGURE 3. Optical microscope images of active area of the transistors encapsulated with photoresist before and after low T hydrogenation process in linear and focused plasma.

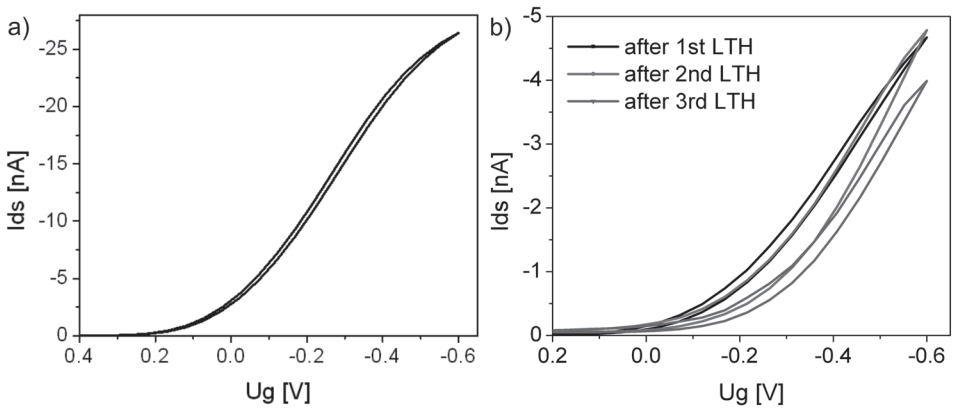

FIGURE 4. (a) Initial transistor characteristic. (b) Transistor characteristics after repeated LTH process in linear plasma at 200 °C. All transfer characteristics were measured in HEPES at $U_{ds} = -0.6$ V.

the fact that transistors characteristics were measured in buffer solution which should maintain stable surface conditions. Origin of these Ut fluctuations is still unknown. Fluctuations after standard hydrogen termination (600 °C) as well as after LTH in focused plasma can not be investigated because covering resists are removed during these processes and thus transistor characteristics cannot be measured.

4. Conclusion

We showed that low temperature hydrogenation at linear plasma system is more suitable due to larger distance between the high-density plasma region and the sample surface. We observed that low temperature hydrogen termination in linear antenna plasma is less aggressive on encapsulation than focused plasma. It kept the similar electronic quality (yet reduced thickness) of covering encapsulation and gold contacts. However, the currents measured after this treatment are lower compared to the focused plasma. When LTH was repeated on the same device we observed fluctuations of threshold voltage Ut within about 150 mV. Origin of these U_t fluctuations is still unknown. Yet, diamond SGFETs are fully operational after this treatment. Therefore, 3D diamond transistors including the encapsulation and gold contacts can be recycled by low temperature hydrogenation in linear antenna reactor within 30 minutes without any other processing.

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