# *Methods to characterize high system resistances of an in glass encapsulated graphene pressure sensor*


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**In an earlier work, a pressure sensor with single-layer graphene encapsulated in glass was realized. The total resistance of the system is many times greater than the sensor response when deflected. In order to exhaust the method of integrating graphene in glass in future novel systems, the high system resistance has to be reduced. Causes for the high resistance need to be detected and characterized, to achieve a decrease of the sensor resistance. The initial step was to measure the influence of the encapsulation process on the used gold contacts. Following, the condition of the embodied graphene was investigated with a laser scanning microscope. Last, possible residuals and impurities at the graphene/metal junction were inspected with the help of XPS-measurements. The study has shown, that the used pressing process increases the resistance of the gold connection, but not to the point, where the problems are fully explained. In addition, the graphene on the inside seems to be in a functional state. Residuals of copper, chlorine, oxygen and tin have been detected. Their influence on the resistance still has to be characterized. The results explain to some degree the high system resistance and address where more research has to be conducted. Future steps will be, to fully characterize the influence of adjacent materials on graphene and consequently, to improve the conductivity of the sensor.**



***Keywords— Single-layer graphene; pressure sensor; encapsulated graphene; glass; contact resistance; graphene/gold junction***


## I. INTRODUCTION

In the year 2004, graphene, the first two-dimensional material, was experimentally synthesized by the two scientists Novoselov and Geim [1]. Even though 80 years ago the thought of free-standing graphene was only a dream and not possible, so the prediction of Landau and Peierls, who stated, that 2D crystals were thermodynamically unstable and could not exist [2], graphene now has a large influence on the scientific world with over 17,000 paper per year [3]. Today there exist, besides the micromechanical cleavage first used by Novoselov and Geim [1], several different methods to synthesize SLG (single layer graphene) samples with diagonals up to 76 cm [4], [5].

The reason for graphene's popularity among scientists worldwide, is due to the extraordinary characteristics it has. Graphene is a semiconductor with no bandgap. For that reason, it's quasiparticles behave like massless relativistic particles with their velocity affiliated to that of the speed of light [6]. This allows, charge carrier mobilities in graphene up to 250,000 $cm^2$ / V * s at room temperature [7]. Furthermore, it has a high Young's modulus of 1 TPa [8], is 97.4 % transparent for visible light [5], because of its 0.34 nm layer thickness [9] and has a high thermal conductivity of 5300 W / m * K [7].

Not only its unique properties make graphene such a fascinating research object, but the diversity of them combined in one material. Graphene has been studied in many different scientific fields. There are a lot of works on NEMS (nanoelectromechanical systems), optoelectronic devices, field-effect transistors and many more potential novel graphene devices [7], [10], [11].

However, graphene possesses one additional major characteristic which occurs to be a problem in many of the listed research fields, especially considering graphene sensors. Due to its 2D-nature graphene only consists of surface area. Therefore, all its unique properties are defined by the condition of the graphene surface. The surface of a material is always in contact with its environment, which may interact and alters it. In the case of graphene, this would mean, that every change of the environmental conditions could shift its properties. Considering for example a gas pressure sensor system on basis of a graphene membrane, the interactions with the gas could alter the properties of the graphene membrane and as a result the behavior of the sensor system altogether. In order to ensure consistent graphene properties and the functionality of graphene-based systems, an encapsulation which preserves the characteristics and protects them from environmental influences is indispensable [12].

In an earlier work, in order to achieve and test such a protecting encapsulation, a 1 $cm^2$ SLG sheet was integrated between two 0.7 mm borosilicate glass plates and permanently joined together by pressing with high temperature and force. The graphene in the center serves, due to its piezoresistive effect, as a pressure sensor, when the whole system gets bent. A connection from the outside to the graphene was given via gold lines on top of a thin chrome layer underneath. The chrome functions as an adhesive layer between glass and gold. To have a spare one, there are always two contacts per edge. A lift-off-process was used to structure the contacts [13]. The

schematic design of the sensor is given in figure 1. The project with the name graphene in glass (GIG), carried out by the Deggendorf Institute of Technology at the technology campus Teisnach, achieved to encapsulate graphene between glass and to preserve it from environmental influences. However, the measured system resistance (~ 200.000 Ω) was very high in comparison to the measured resistance change contributed by the piezoresistive effect (~ 440 Ω). The lack of its advantageous properties, like high carrier mobility or a distinct piezoresistive effect, as shown in other works [14], makes the graphene pressure sensor not viable for the use in future novel systems.

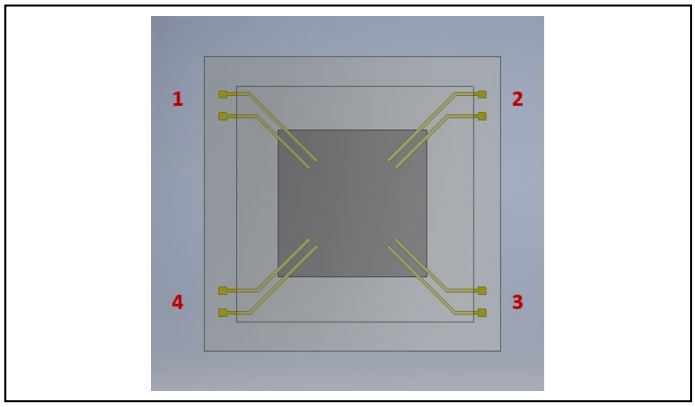


Fig. 1. Schematic picture of the graphene pressure sensor with graphene in the middle, encapsulated in glass and contacted via gold line

In this paper, the causes for the high resistance of the sensor system are investigated, in order to solve the problem with the minor ratio of the sensor response to the total sensor resistance. With overcoming the challenge of encapsulating graphene in glass and preserving its beneficial properties, new possibilities to integrate and use graphene in future NEMS, optoelectronic systems, etc. would be generated.

In consideration of the manufacturing process, probably three different indicators for the high resistance are possible. The first two possible complications could be caused due to the high temperature and pressure force during the pressing cycle. On the one hand, it is possible, that the contacts got altered or damaged and on the other hand the graphene on the inside may have taken harm. The third aspect which was looked into are possible residuals and impurities between the graphene and metal contacts after previous process steps.

## II. Used Methods

### A. *Influence of the pressing process on the contacts*

To encapsulate the graphene between the two borosilicate glasses, the glass press modeling machine Nanotech 140 GPM from Moore Nanotechnology Systems LLC is used. During the pressing cycle, the sensor is heated to 625 °C and gets pressed with a force of 5 kN which is held for 120 s. It is fair to suspect, that the high force and temperature could have damaged or altered the gold contacts. Especially the edges of the top glass could have cut through the gold/chrome layer. To investigate the influence of the pressing process on the contacts, the graphene was replaced with a ~ 21 nm thick gold layer. The gold was sputtered on the glass for 30 s with the Quorum Q 300 TD. The gold layer in the middle of the sensor should form a good connection with the contacts. Therefore, a change of the system resistance after the pressing process would only be attributed by a change of the contacts itself. In order to evaluate this, the resistance was measured between each contact with a digital multimeter before and after the pressing process. In total, two gold-sensors were created. For one of them, an $O_2$-clean was carried out before adding the gold square in the middle. (Before transferring the graphene on the sensor, in order to clean the surface and to make it hydrophile for the transferring process, an $O_2$-clean is performed.) Having only one of the samples cleaned, it is possible to simultaneously check if the pretreatment of the sensor influences the gold contacts. For the clean, the plasma surface treatment machine Tetra 30 LF – Diener was used. The $O_2$ gas flow was at 200 sccm with a pressure of 0.45 mbar. The generated oxygen ions were accelerated with a voltage of 60 W. The cleaning process had a duration of 10 s. Additionally, a van-der-pauw-measurement was conducted [15]. This method allowed, to determine the specific resistance of the gold sheet after the pressing process and to see if the gold-layer got damaged. For the van-der-pauw-measurement, the source-meter Keithley 2450 was used. The system was set to resistance measuring mode and during the four-wire-measurement, a current of 100 µA was imprinted onto the gold substrate.

### B. *Inspection of the graphene layer after the pressing process*

The results from the previous work have shown, that the graphene successfully connects the gold contacts and that a piezoresistive effect is present and measurable. However, the high system resistance could be an indication of harm to the graphene due to the pressing process. In the case of graphene, using the van-der-pauw-method to determine the specific resistance of the graphene sheet, comparing it to know values in the literature and to see if it is unarmed, is not possible. Due to the earlier mentioned problem, that SLG changes its properties depending on the environmental circumstance, it's not possible to say, what the "correct" specific resistance of the graphene between the two glass plates should be. Therefore, it was decided to analyze the graphene condition by the means of an optical investigation method.

Raman spectroscopy is shown to be able to detect graphene and would normally be the first choice to characterize its constitution [16], [17]. However, for a large area scan like in this case (1 $cm^2$), the investigation with a Raman spectrometer would take a huge amount of time. Therefore, the laser scanning microscope (LSM) Olympus LEXT OLS4100 was used. For the image the laser was operated with a wavelength of 405 nm and a 5x objective was used. The complete image (Fig. 4) consists of several smaller images and was joined together via the software of the LSM.

### C. *XPS analysis of graphene/metal junction*

A major influence on the resistance of the whole sensor system has the graphene/metal junction. The quality of it is defined by a variety of different factors. One of those aspects is, that the current flow path of a metal/graphene junction doesn't include the whole contact area. Instead the current flows over the edges of the junction [18]. Another one correlates with the above-mentioned statement, that the properties of graphene changes with its environmental influences [12]. Residuals or impurities between the graphene and gold contact, would reduce the usable area for the electron flow and probably influence the electrical properties of the graphene. For instance, it is known that residuals from photoresists often lead to high resistances [19]. Therefore, to determine, the existence of impurities, in what quantity they occur and how extensive their influence is, a throughout investigation of all the components in the gold/graphene junction area is necessary. In order to measure the composition of the junction, a depth scan with an XPS and an angle-resolved x-ray photoelectron spectrum (ARXPS) was conducted.

For the XPS measurements, the graphene was placed on top of the larger outer gold contacts and not in the middle, to have a vaster area for the measurement. The used spectrometer is the NEXSA from Thermo Fisher Scientific. Excitation was done by monochromatic Al-$K_\alpha$ radiation (1486,6 eV) with a 400 µm beam diameter. The sample was simultaneously flooded with low energetic electrons and Ar-ions for charge compensation. Survey spectra were recorded with a pass energy of 200 eV, detail spectra with a pass energy of 50 eV and averaging over 5 scans. Very slow sputtering for the depth profile was achieved with a MAGCIS cluster gun. The argon cluster size was 1000 atoms, which were accelerated with an energy of 4 keV. The first measurement is a surface spectrum of the graphene/gold junction. Following, a depth profile with an etch time of 160 s was generated. The third spectrum is an ARXPS measurement consisting of nine scans in an angle range from 0 ° - 80 ° with a step size of 10 °. Each angle was measured ten times with a dwell time of 0.1 s, the final spectrum is a result of the ten measurements. Additionally, the surfaces of the used glass plates were measured, because of possible differences due to their manufacturing process.

## III. Results and Discussion

### A. *Conductivity change in the gold contacts*

Resistance measurements of both substrates, before and after pressing, has shown, that the gold samples have a significantly lower resistance than the graphene sensor. The two gold sensors also display an increase in contact resistance after the pressing process. The sample without $O_2$-clean has an average resistance of 91 Ω before pressing and 486 Ω after pressing (see Fig. 2). The one with the $O_2$-clean shows a slightly higher increase of the average resistance from 90 Ω before to 1319 Ω after pressing (see Fig. 3). The resistances of the four-wire-measurement results in 0.27 Ω when the current is imprinted between the contacts [1;2] and 0.18 Ω between [1;4]. With this, the van-der-pauw-measurement concludes in a specific resistance for the gold sheet of 2.14 * $10^{-8}$ Ω * m² / m.

The value for the specific resistance of the gold square is in accordance with values in the literature [20]. Therefore, the pressing process doesn't seem to affect the gold in the center of the sensor. However, both sensors show an increase in their total resistance. The resistance of the sample without the $O_2$-clean is five times higher and the resistance of the sample with $O_2$-clean is almost 15 times higher after pressing. This shows, that the pressing process influences the high resistance of the graphene sensor. Knowing that the gold in the center is unharmed, means, only the gold lines connecting the contacts with the graphene are influenced by the pressing process. An explanation could be, that the gold lines get damaged by the edges of the top glass but don't completely get cut off. Seeing that this has been the case for all the contacts, and none got cut off, leaves room for another interpretation. Due to the high force and temperature the chrome underneath interacted with the gold lines, altering the conductivity of the contacts. Further measurements are needed to be certain, what causes this resistance increase. The same goes for the difference in resistance increase of the $O_2$-cleaned sample. The treatment could influence the different increase of both samples. However, for now, it's not possible to say what would cause this effect or if it is just a coincidence. One aspect for the increase of the total resistance of the graphene sensor was found. Nonetheless, it only explains a modest increase in comparison to the extensive 200,000 Ω resistance and further reasons for it have to exist.

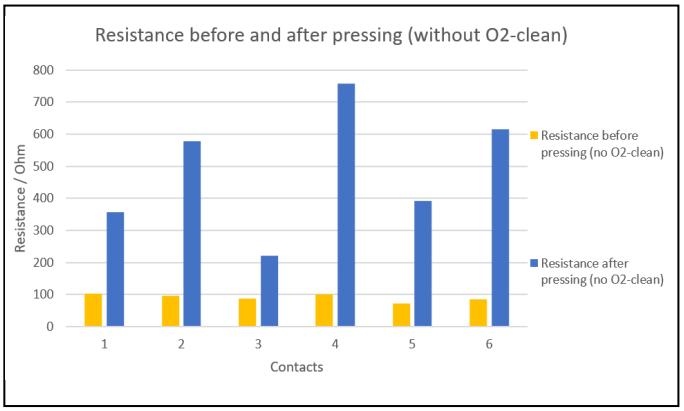


Fig. 2. Measurement of the gold sensor without $O_2$-clean.

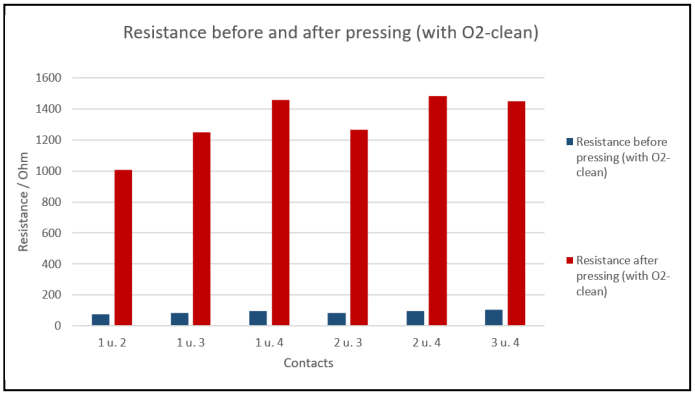


Fig. 3. Measurement of the gold sensor with $O_2$-clean.

### B. *Surface inspection of encapsulated graphene*

Graphene's unlimited thinness makes it a challenging task to detect it with an analyzing method of any kind. Furthermore, it is encapsulated between two glass plates with a thickness of 0.7 mm. Therefore, focusing on the graphene with an LSM and obtaining an image of the graphene wasn't trivial. However, figure 4 shows, that it is possible to depict graphene between two glass layers with an LSM. Even more, it is possible to create a good contrast and to be able to clearly differentiate the transition from glass to graphene. The graphene in the image doesn't display any major holes or defects. The edges are slightly frayed, yet, it's not possible to determine if the pressing process caused this or an earlier production step. In the bottom left corner, some holes can be detected. However, they are suspected to don't influence the measured resistance because they lay behind the gold contacts. As far as the resolution of the image allows it, the graphene layer seems to be in a functional condition and the encapsulation process successful. Yet, it has to be mentioned, even though the graphene could clearly be identified between the two glass plates and a good contrast in comparison to the underlying platform was created, the large area scan doesn't allow to determine if micro or nanoholes were created by the pressing process. In order to detect such defects, very detailed and time-consuming Raman microscope measurements would be required. Before using this method, other possible causes for the high resistance shall be conducted and their results are to be awaited first.

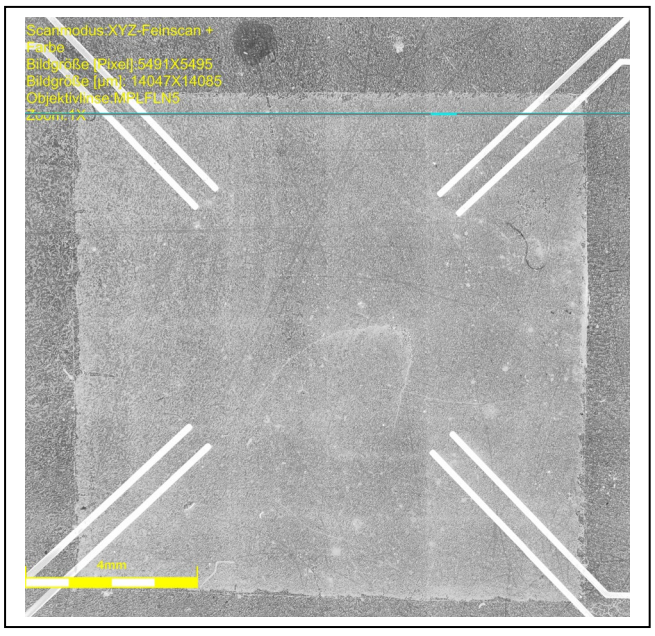


Fig. 4. Laser scanning microscope image of the encapsulated graphene

### C. *Residuals between graphene and gold contacts*

The first XPS overview measurement of the graphene/gold junction (Fig. 5A) shows the components of the connection. Three significant peaks of gold, carbon and oxygen were detected. The gold peak Au4d5 is at a binding energy of 335.2 eV with an atomic proportion of 12.5 %. The most present one is the C1s carbon peak at 285.1 eV with 72.0 % and the oxygen peak O1s was detected at 532.7 eV with a percentage of 13.33 %. Furthermore, two additional smaller peaks could be observed. A Cl2p chlorine peak at 200.1 eV with 1.9 % and a Cu2p3 copper peak at 936.2 eV with a percentage of 0.3 %. In figure 5B1 the depth profile of the said peaks is given. The carbon concentration starts at 72 % and declines with the time until 25 %, while the gold line simultaneously gets more present (12.5 % - 57 %). Furthermore, a continuous level of oxygen at about 14 % seems to be present. Figure 5B2 shows an enlarged cut out of figure 5B1, were the chlorine and copper progress is portrayed. The copper is almost nonexistent at the beginning and grows soon to a nearly continuous level of about 1.8 %. The chlorine drops from 2 % to 0 % and then starts to alternate. The result from the ARXPS-measurement (Fig. 5C) also shows that oxygen is present and that it is the topmost layer. However, no information is given about its depth distribution. Copper and chloride weren't detected probably because of their minor occurrence. The XPS overview measurement of the borosilicate glass (Fig. 5D) shows the difference between its front- and backside. The red spectrum displays major differences at certain binding energies, because of the detected tin.

The tin layer can be explained due to the production process of the borosilicate glasses. The float glass is cooled on a tin bath in order to achieve a smooth surface. It seems, that few tin particles still reside on the glass backside. Therefore, the contamination can only be found on one side of the glass. Further measurements are needed, to determine the influence of the tin on the graphene properties.

The decreasing carbon concentration belongs to the SLG sheet which gets etched away after time. Underneath lay the gold contacts which become more persistent while the graphene decreases. Small parts of oxygen could still reside on the surface of the graphene sheet, after the transferring process in water. The oxygen on top of the gold contacts exist probably due to the $O_2$-clean. This would explain the continuous level of oxygen throughout the measurement. The copper and chlorine portions can be explained due to the production process of the graphene. The in this project used graphene gets grown on copper foil with the use of chemical vapor deposition (CVP). In order to separate the graphene from the copper, an etchant consisting of $FeCl_3$ is used. Thus, residuals of chlorine and copper are still on the graphene. The increase of the copper concentration is explained by the fact, that the bottom side of the graphene, is the side where the copper was etched away. The alternating chlorine distribution probably lies in the fact, that the concentration was partwise to small to be recognized. Normally, also Fe residuals would be found on the graphene. In this case, it seems, that its concentration was too low to be detected. These residuals can influence the electronic behavior of the encapsulated graphene, probably leading to a worse graphene/gold connection [21]. The exact influence on the system resistance has to be investigated in the future.

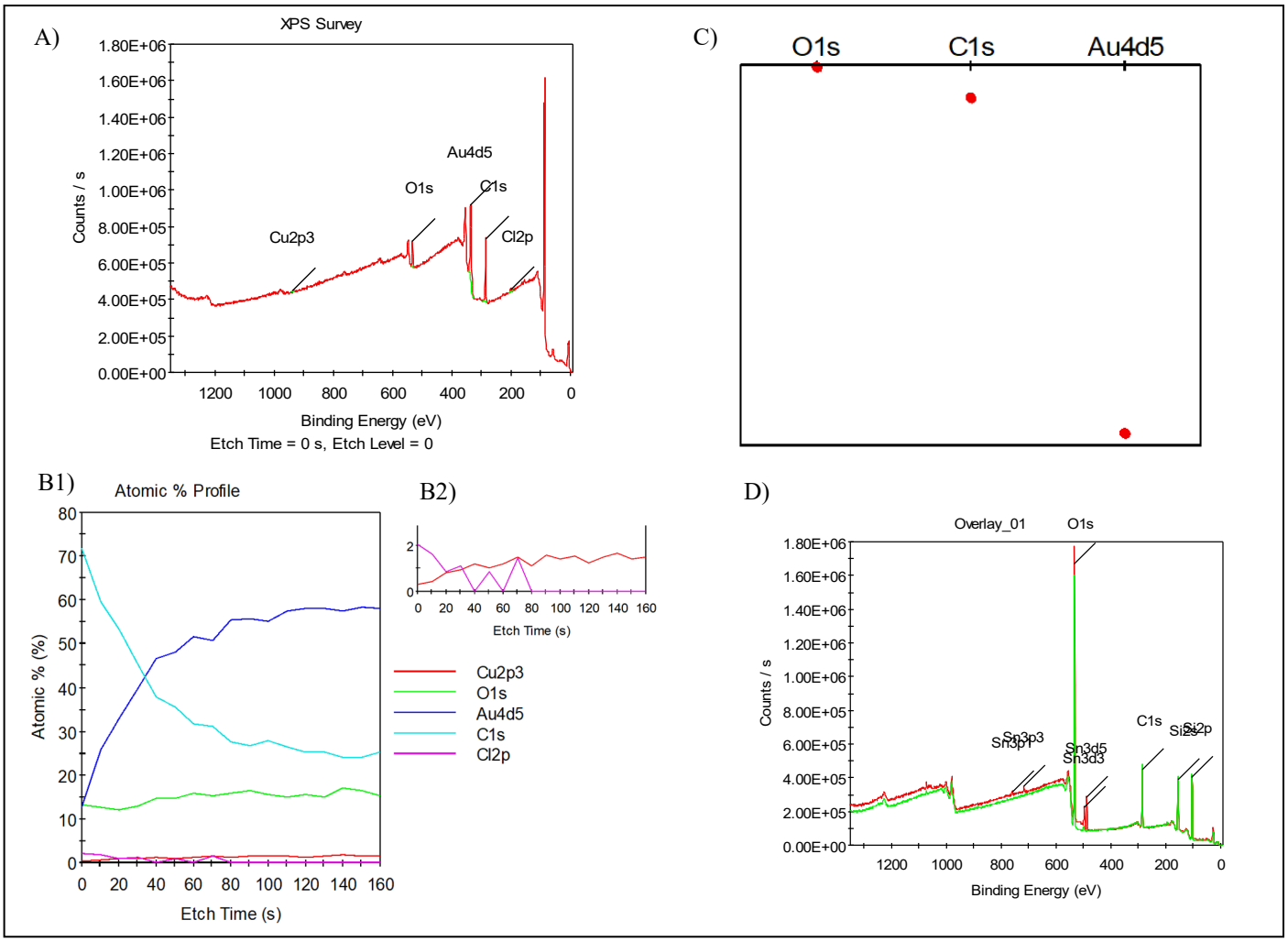


Fig. 5. A) XPS-survey spectra of the components at the graphene/gold junction; B1) Depth profile of the junction deposition with an etch time of 160 s; B2) Enlarged cut out of the depth profile, focused on the progress of the copper and chlorine concentration; C) Relative depth plot of the ARXPS-survey on the graphene/gold junction, measured over nine different angles; D) XPS-measurement of the borosilicate glass. In red, the spectrum with the tin contamination on the glass, in green, the spectrum of the opposite glass surface.

## IV. Conclusion

Three different aspects were investigated, which probably influence the system resistance of the pressure sensor with graphene encapsulated in glass. It was disclosed, that the high temperature and force of the pressing process have a worsening effect on the conductivity of the gold contacts. Using LSM, a fast way to observe encapsulated graphene between glass was discovered. The graphene also seemed to be in a functional condition. The third aspect was the investigation of the graphene/gold junction. Residuals of copper, chlorine and oxygen were detected. Cu and Cl probably have a negative influence on the electronic properties of graphene. Concluding, the project managed to determine several aspects that influence the resistance of the graphene sensor. However, the change in the gold contact connectivity is too little to explain the measured system resistance. Additionally, for the influence of the impurities between gold and graphene, a detailed characterization has still to be done. This quest needs to be addressed in future works, in order to successfully integrate graphene in glass and therefore in novel systems.

## References


[1] K. S. Novoselov, „Electric Field Effect in Atomically Thin Carbon Films“, Science, Bd. 306, Nr. 5696, S. 666–669, Okt. 2004, doi: 10.1126/science.1102896.

[2] A. K. Geim und K. S. Novoselov, „The rise of graphene“, Nature Materials, Bd. 6, S. 183, März 2007.

[3] L. Zou, L. Wang, Y. Wu, C. Ma, S. Yu, und X. Liu, „Trends Analysis of Graphene Research and Development“, Journal of Data and Information Science, Bd. 3, Nr. 1, S. 82–100, März 2018, doi: 10.2478/jdis-2018-0005.

[4] J. Phiri, P. Gane, und T. C. Maloney, „General overview of graphene: Production, properties and application in polymer composites“, Materials Science and Engineering: B, Bd. 215, S. 9–28, Jan. 2017, doi: 10.1016/j.mseb.2016.10.004.

[5] S. Bae u. a., „Roll-to-roll production of 30-inch graphene films for transparent electrodes“, Nature Nanotechnology, Bd. 5, Nr. 8, S. 574–578, Aug. 2010, doi: 10.1038/nnano.2010.132.

[6] K. S. Novoselov u. a., „Electronic properties of graphene“, physica status solidi (b), Bd. 244, Nr. 11, S. 4106–4111, Nov. 2007, doi: 10.1002/pssb.200776208.

[7] A. C. Ferrari u. a., „Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems“, Nanoscale, Bd. 7, Nr. 11, S. 4598–4810, 2015, doi: 10.1039/C4NR01600A.

[8] J.-W. Jiang, J.-S. Wang, und B. Li, „Young's modulus of graphene: A molecular dynamics study“, Phys. Rev. B, Bd. 80, Nr. 11, S. 113405, Sep. 2009, doi: 10.1103/PhysRevB.80.113405.

[9] D. G. Papageorgiou, I. A. Kinloch, und R. J. Young, „Mechanical properties of graphene and graphene-based nanocomposites“, Progress in Materials Science, Bd. 90, S. 75–127, Okt. 2017, doi: 10.1016/j.pmatsci.2017.07.004.

[10] A. D. Smith u. a., „Electromechanical Piezoresistive Sensing in Suspended Graphene Membranes“, Nano Letters, Bd. 13, Nr. 7, S. 3237–3242, Juli 2013, doi: 10.1021/nl401352k.

[11] M. Wang, C. Yan, und L. M, „Graphene Nanocomposites“, in Composites and Their Properties, N. Hu, Hrsg. InTech, 2012.

[12] G. Ruhl, S. Wittmann, M. Koenig, und D. Neumaier, „The integration of graphene into microelectronic devices“, Beilstein Journal of Nanotechnology, Bd. 8, Nr. 1, S. 1056–1064, Mai 2017, doi: 10.3762/bjnano.8.107.

[13] MicroChemicals, „User manual ‚LOR and PMGI Resists'“, S. 7.

[14] X.-W. Fu u. a., „Strain dependent resistance in chemical vapor deposition grown graphene“, Applied Physics Letters, Bd. 99, Nr. 21, S. 213107, Nov. 2011, doi: 10.1063/1.3663969.

[15] Prachurya Bharadwaj, „Van der Pauw Resisitivity Measurement“, Unpublished, 2017, doi: 10.13140/rg.2.2.23468.67208.

[16] A. C. Ferrari und D. M. Basko, „Raman spectroscopy as a versatile tool for studying the properties of graphene“, Nature Nanotechnology, Bd. 8, Nr. 4, S. 235–246, Apr. 2013, doi: 10.1038/nnano.2013.46.

[17] R. Beams, L. Gustavo Cançado, und L. Novotny, „Raman characterization of defects and dopants in graphene“, J. Phys.: Condens. Matter, Bd. 27, Nr. 8, S. 083002, März 2015, doi: 10.1088/0953-8984/27/8/083002.

[18] K. Nagashio, T. Nishimura, K. Kita, und A. Toriumi, „Contact resistivity and current flow path at metal/graphene contact“, Appl. Phys. Lett., Bd. 97, Nr. 14, S. 143514, Okt. 2010, doi: 10.1063/1.3491804.

[19] T. Cusati u. a., „Electrical properties of graphene-metal contacts“, Sci Rep, Bd. 7, Nr. 1, S. 5109, Dez. 2017, doi: 10.1038/s41598-017-05069-7.

[20] J. R. Rumble, D. R. Lide, und T. J. Bruno, CRC handbook of chemistry and physics: a ready-reference book of chemical and physical data. 99th Edition. 2018.

[21] A. Ambrosi und M. Pumera, „The CVD graphene transfer procedure introduces metallic impurities which alter the graphene electrochemical properties“, Nanoscale, Bd. 6, Nr. 1, S. 472–476, 2014, doi: 10.1039/C3NR05230C.