# Vertical Graphene Growth by PECVD

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## Definition

Vertical graphene, which belongs to nanomaterials, is a very promising tool for improving the useful properties of long-used and proven materials. Since the growth of vertical graphene is different on each base material and has specific deposition setting parameters, it is necessary to examine each base material separately.

## 1. Introduction

Among nanomaterials, graphene is one of the most studied materials due to its strong chemical bond between individual atoms, which gives it exceptional mechanical properties. Although graphene was discovered in 2004, the main problem, as with any new technology, is the price, depending on the quality of the final product. In the first years after its discovery, it was one of the most expensive materials in the world, but this situation has changed over the course of 15 years due to the discovery of new production processes[1].

Graphene has excellent electrical properties, while the charge mobility in a perfect graphene monolayer can reach a theoretical value of up to 200,000 cm2 V−1 s−1[2]. The resistivity of the resulting layer would be at room temperature 10−6 Ω cm and would make graphene the best electrical conductor. In terms of mechanical properties, graphene has a tensile strength of 130 GPa [3]and a Young's modulus value of 1 TPa [4], which makes it the strongest material in the world.

Depending on the plasma-enhanced chemical vapor deposition (PECVD) setting, graphene growth can be either horizontal or vertical. The advantage of vertical graphene is mainly its large active area, which is used mainly in the production of biosensors, batteries, capacitors, electric field sources, or catalysts [4][5][6].

AlCu4Mg aluminum alloy is a very machinable material that can be polished, has a low weight, but is difficult to weld. It has poorer corrosion resistance and anodizability. It is suitable for hot and cold forming (forging). It has high strength, while in the hardened state the tensile strength is 400 MPa and the hardness is 100 HB. It is the most widely used aluminum alloy for forming, it is used in the automotive and aerospace industries for components that operate at room temperature. Another wide area of its use is the packaging industry.

The growth of graphene depends on the base material on which its occurrence is needed. Long-term used and proven materials can be further improved by the myriad benefits that graphene offers. Since the growth of graphene is different on each material and has specific deposition setting parameters, it is necessary to examine each base material separately. The aluminum alloy AlCu4Mg, which is the subject of this study, is used as the basic material for graphene growth for the very first time and has not been investigated in any presented study so far. The AlCu4Mg aluminum alloy, which is now used mainly in the packaging industry, has great potential for future use with the graphene coating. This alloy is widely used for the production of packaging in the food industry, and any improvement in the process will bring significant benefits due to the fact that it is a mass production worldwide. This study not only provides theoretical knowledge about the growth of vertical graphene on this aluminum alloy, but also has a promising potential for use in the packaging industry.

## 2. Experimental Method

### 2.1. Preparation of Vertical Graphene

The substrate in the form of sheet metal of thickness 0.1 mm from the material AlCu4Mg, whose chemical composition in weight percentages given by the standard is 4.3% Cu, 0.79% Mg, 0.26% Fe, 0.24% Si, 0.3% Mn, 0.04% Ti, 0.04% Zn, Al-balance was divided into individual samples measuring 10 × 10 $mm^2$

using a laser cutter (Laser Dicer Oxford Lasers A-Series, Oxfordshire, UK). Individual samples were purified with acetone, isopropyl alcohol, and deionized water before being placed in a PECVD chamber (Oxford Nanofab, Oxfordshire, UK). An RF source with a frequency of 13.56 MHz was used as the plasma source, and after inserting the sample into the PECVD chamber of the instrument, the temperature increased at a rate of 27 °C/min up to the target temperature. After reaching the target temperature, annealing was performed in a hydrogen atmosphere for 15 min. This was followed by the deposition of vertical graphene alone, which lasted 45 min and was performed in an atmosphere with different concentrations of hydrogen and methane. After deposition, the temperature in the chamber was reduced to 695 °C, at which the sample could be transferred to the loading chamber, where it was cooled to room temperature. The parameters of individual depositions were set according to the design of experiment, which is described in detail in the following chapter.

### 2.2. Performed Design of Experiment

The input factors of the experiment were Temperature (°C), Pressure (mTorr), Flow (sccm), $CH_4$ (%), Plasma power (W), and Annealing in $H_2$ (sccm). These factors have been selected based on previous studies on the growth of vertical graphene, such as Zhao, Chugh [8], or Bo [9]. A full factor design of experiment with $2^6 = 64$ rounds was compiled, which contained additional 5 central points, i.e., a total of 69 rounds of individual experiments. The central points were used to determine the repeatability of the experiment. The thickness of the superimposed vertical graphene was used as the response function of the system. In case of graphene occurrence in less than 50%, binary logistic regression with binary response in the form of occurrence/non-occurrence of vertical graphene will be used for evaluation instead of linear regression.

### 2.3. Experimental Methods

Atomic force microscope (AFM) of a Dimension Icon type from BRUKER (Billerica, MA, USA) set in tapping mode equipped with an ultra-sharp FIB -100 tip was used to visualize 2D and 3D surface topography, and the measured data were analyzed in Gwyddion software (CEITEC – Central European Institute of Technology, Brno University of Technology, Brno, Czech Republic). Imaging of vertical graphene and measuring its thickness was made possible using a Helios-type electron microscope from THERMO FISHER (Hillsboro, OR, USA), which was equipped with a focused ion beam (FIB) and with an energy-dispersive X-ray detector (EDX). A Titanium transmission electron microscope (TEM) from THERMO FISHER (Hillsboro, OR, USA), with an accelerating voltage of 30 kV was used to image graphene in atomic resolution. Raman spectroscopy performed on a Raman inVia Microscope from RENISHAW (controlled by WiRE 3.4 software, Renishaw plc, Wotton-under-Edge[11][10], UK) equipped with a laser with a wavelength of 514 nm, a 100 × objective lens with 10 s of signal accumulation was used to determine the quality of individual graphene samples. The power of the laser beam during the measurement was constantly set to 10 mW.

## 3. Conclusions

The analysis of the growth of vertical graphene on the aluminum alloy AlCu4Mg using PECVD technology was performed using a design of experiment of 69 rounds, followed by an evaluation of its growth and further analysis, which reached the following conclusions:

After performing the design of the experiment, it was found that the growth of vertical graphene occurred in only 7 cases, always when setting the parameter Temperature to 800 °C, Pressure to 200 mTorr and CH4 to 100%, while the other three parameters Flow, Plasma power, and Annealing in H2 were different, The highest thickness of 310 nm was reached for Sample 54 (Flow 100 sccm, Plasma power 300 W, and Annealing in H2 150 sccm) and, conversely, the lowest thickness for Sample 50 (Flow 100 sccm, Plasma power 300 W and Annealing in H2 30 sccm) and only 146 nm, Imaging of deposited vertical graphene was performed using AFM, SEM, and TEM, Raman spectroscopy showed the deposition of vertical graphene in all 7 cases of its growth and in the Raman spectrum, in addition to standard graphene peaks (G, 2D), several additional ones were discovered, which were D, D + D′, and D + D″ and also D′, D″, A comparison of the data for the different values of the Power parameter shows that a higher value of the plasma power reduces the 2D/G ratio, which is related to the higher energy of the system during deposition, A regression model was created describing about 90% of the variability of the monitored graphene thicknesses, while only the Flow (sccm) interaction is statistically significant × Pretreatment H2 (sccm).

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## Keywords

vertical graphene;PECVD;aluminum alloy;AlCu4Mg