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Cite as: AIP Conference Proceedings **2380**, 040008 (2021); <https://doi.org/10.1063/5.0058246>  
Published Online: 25 June 2021

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# Direct Graphene Growth on GaN and Au Materials Using the PECVD Method

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**Abstract.** The great interest in graphene applications in optics and optoelectronics still requires alternative methods for obtaining high-quality graphene. Currently used methods are based on graphene transfer onto a target substrate. As a consequence, the structural quality of graphene is lowered and so are its the electrical and optical properties. What is more, the transferred graphene layer is often contaminated with Cu, Ge or chemical residue. As a result, such a graphene layer can only be used in limited applications. Better quality is required when the 2D material is to be applied as a transparent conductive electrode (TCE) in a GaN-based light emitter or as an active layer in an Au-containing optical fibre. Therefore, alternative methods for graphene deposition are still in demand. In this work, a plasma-enhanced chemical vapour deposition (PECVD) process was used for direct graphene growth on GaN and Au substrates in the Aixtron Black Magic system. This method does not require chemical isolation, graphene transfer or a metallic catalyst. The entire process can be conducted in stable and repeatable conditions. Structural homogeneity of obtained graphene was observed using scanning electron microscopy. Its presence and overall optical characteristics were investigated with Raman spectroscopy over a large area (mapping mode). They confirmed the formation of graphene and its dependence on growth time through the presence of the 2D mode. The results prove that PECVD is a promising method for obtaining graphene in the form of flakes.

## INTRODUCTION

Graphene remains one of the major areas of interest in the field of optics and optoelectronics. There are a lot of scientific works concerning graphene as a transparent conductive electrode (TCE) intended to homogeneously spread current over the surface of a semiconductor-based light-emitting diode (LED). Among semiconductors, gallium nitride (GaN) is one of the most widely used for LEDs, and implementation of graphene into GaN-based LEDs technology is currently under study. Literature reports that homogeneous spreading of current across the surface would improve the efficiency of GaN LEDs by solving the challenge of improper ohmic contact formed through conventional metallisation [1]. However, to date, only a limited number of studies concerning graphene growth directly on GaN have been published. Moreover, there is uncertainty as to the nature of growth and the obtained layers are of questionable quality. Little is also known about graphene growth directly on gold (Au) and it is not clear what factors are responsible for the growth mechanism and the nature of the graphene-Au connection. One of the critical factors of growing graphene on Au, is the lack of catalytic activity of the substrate. Despite the low activity of Au surface, Ozguluer et al. reported successful direct growth of graphene on Au. They analysed the carbon solubility

differences in Au and other commonly used metallic substrates, such as copper (Cu) and nickel (Ni). Also, they noticed that carbon solubility in Au is higher than in Cu, but lower than in Ni. On this basis, they postulated that the mechanism of CVD growth of graphene on Au can be similar to the one on Cu substrate. Nevertheless, the development of direct graphene growth on Au remains unclear. Still, literature reports a great potential of graphene-Au components in spectroscopy [2] and electrochemistry [3, 4]. Also, the graphene/Au combination has a potential in optical fibres technology [5]. As far as optical applications are concerned a quality graphene layer with high electrical conductivity and high transmittance in a broad wavelength range is strongly required. Despite the development of various manufacturing methods, the main challenge faced by many researchers is to obtain high-quality graphene on various substrates without the need for the use a copper (Cu) or nickel (Ni) catalysts. In literature, the main method of graphene growth is chemical vapour deposition (CVD) on Cu, Ni foils, with the isolation of the graphene layer and final transfer of graphene onto the target substrate [6]. This method suffers from a high probability of damage to the graphene layer via wrinkles, holes, overlapping, and chemical residues, which can affect its electrical and optical properties. Therefore, several attempts have been made to directly grow graphene on various non-metallic substrates, such as sapphire ( $\text{Al}_2\text{O}_3$ ), magnesium oxide ( $\text{MgO}$ ), aluminum nitride ( $\text{AlN}$ ), boron nitride ( $\text{BN}$ ) [7] and gallium nitride ( $\text{GaN}$ ) [9-11]. Also, there is little published data on graphene growth on metallic substrates such as gold (Au). Up to now, the most reported method of graphene growth on GaN and Au is based on the CVD growth on Cu. This concept has been challenged by a few reports [8] indicating, e.g. the degradation of GaN surface at graphene growth conditions such as temperature (above  $900\text{ }^\circ\text{C}$ ) and the presence of  $\text{H}_2$ . It was found that on the surface of the GaN, Ga droplets appear in  $\text{H}_2$  environment at high temperatures [9, 11]. Such degradation precludes the growth of high-quality graphene. The aforementioned reports on the direct growth of graphene on GaN and Au substrates show the importance of developing new deposition methods that will prevent surface degradation and allow graphene growth.

This paper investigates the use of PECVD as an alternative method for direct graphene growth on GaN and Au substrates, which is significant for optoelectronic applications. In the PECVD method, the high-frequency voltage ignites plasma, which allows to excite the gas molecules to an energy compatible with the energy normally obtained with high temperature [12]. Hence, the PECVD provides another source of energy than thermal. For this reason, the growth of graphene under lower temperature is possible. Furthermore, PECVD method enables graphene deposition on a variety of substrates because substrates with a catalytic activeness are not required [13]. These features make this method attractive for a scalable industrial growth of graphene. In the pages that follow, we will be investigating whether the PECVD allows the growth of graphene on GaN and Au and the prevention of the surface degradation at the same time. By employing different growth times during the PECVD we attempted to indicate essential differences in graphene formation as well as the state of the GaN and Au substrates. The surface changes will be monitored structurally via scanning electron and atomic force microscopies. By employing Raman spectroscopy the evaluation of graphene quality will be conducted.

## EXPERIMENTAL SECTION

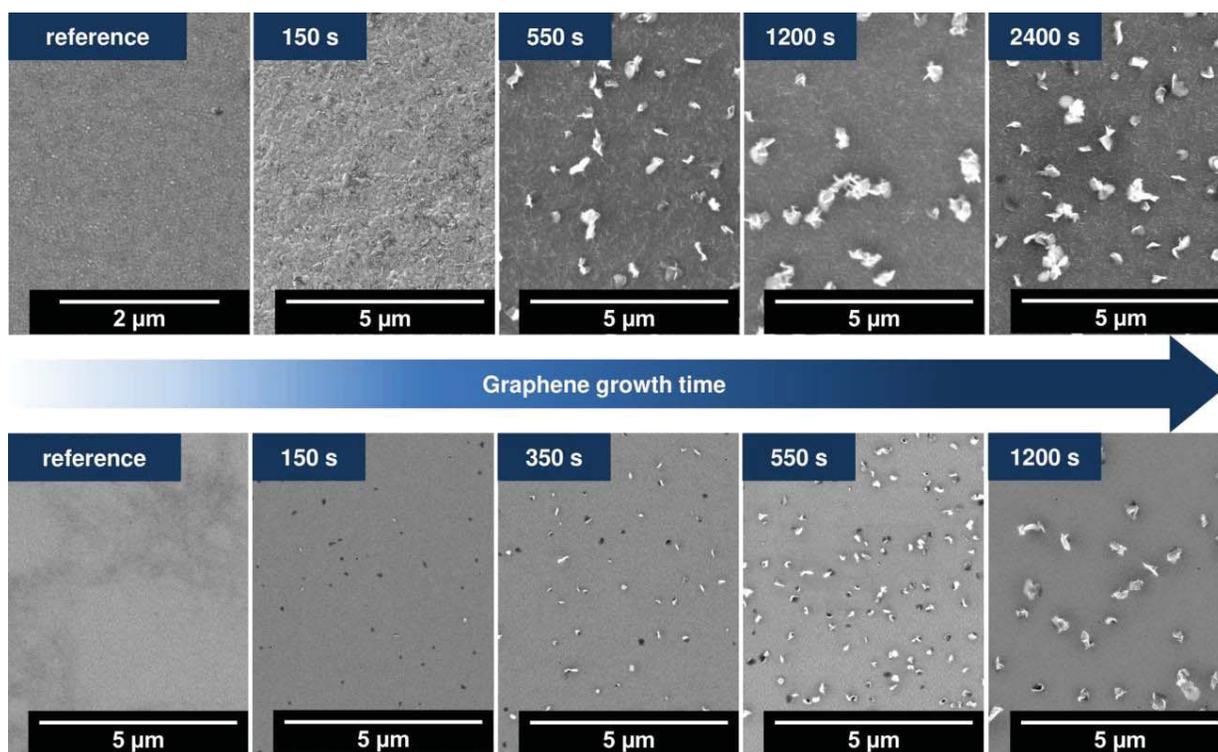
Two types of substrates were chosen for the graphene studies. Substrate (A): 1400-nm highly-resistive gallium nitride epitaxial structure grown on a sapphire substrate ( $\text{HR-GaN/Al}_2\text{O}_3$ ); (B): 20-nm gold layer on a 100-nm chromium layer deposited onto a sapphire substrate ( $\text{Au/Cr/Al}_2\text{O}_3$ ).

The growth of graphene was conducted on the two types of substrates through plasma-enhanced chemical vapor deposition (PECVD) in the Black Magic reactor (model: AIXTRON NanoInstruments SystemPro for 6-inch wafers). Prior to each process the substrates were cleaned with acetone and dried in nitrogen flow. Samples during the process were heated in Ar atmosphere for 30minutes and then etched in  $\text{Ar/H}_2$  gas mixture for 15 minutes to remove particles and smooth out the surface. Growth of the graphene layer was conducted at temperatures:  $500\text{-}600\text{ }^\circ\text{C}$  under pressure:  $2\text{-}5\text{ mbar}$  in  $\text{Ar/H}_2$  atmosphere. Methane was used as carbon source ( $\text{CH}_4$ ) with a flow ratio  $\text{CH}_4\text{:H}_2\text{:Ar}=2\text{:}5\text{:}50$ . To promote graphene growth the plasma frequency during the growth was set at  $15\text{ kHz}$  with the voltage in the range between  $400\text{-}600\text{ V}$ . To discharge the substrate the table was applied negative voltage with  $1\text{-ms}$  pulses. In this work we presented data obtained for samples with the time of graphene growth between  $150\text{ s}$  to  $2400\text{ s}$ .

Samples' surface was studied with different characterisation methods such as: high-resolution SEM imaging with SE+BSE detection mixed signals (HITACHI SU8230), optical profiler equipped with a LED light source (white and green, Bruker ContourGT) and Raman spectroscopy (Renishaw inVia Raman Microscope). To identify the presence and quality of graphene Raman spectra were obtained with a  $532\text{-nm}$  Nd:YAG laser with about  $0.3\text{ }\mu\text{m}$  spot size. Results were analysed with an in-house custom-made software cable of noise filtering, background subtraction, fitting, and finally two-dimensional imaging of the collected spectra.

## RESULTS AND DISCUSSION

The first set of analyses examined the impact of graphene growth conditions on surface changes of the HR-GaN and Au/Cr/Al<sub>2</sub>O<sub>3</sub> substrates. Figure 1 compares SEM micrographs between the reference samples and time-dependent growth of graphene on the HR-GaN and Au/Cr/Al<sub>2</sub>O<sub>3</sub>. While the reference surfaces were optically smooth, the SEM observations after graphene growth revealed that flakes with a bright contrast have occurred. Moreover, some dependence can be observed, that the longer the growth time of graphene, the more and bigger are the flakes visible on the HR-GaN as well as Au/Cr/Al<sub>2</sub>O<sub>3</sub> substrates. However, the observed tendency changes after reaching a threshold corresponding to a specified growth time. Computer image analysis was applied to estimate the size and quantity of flakes that were observed by SEM microscope. The results of this analysis are presented in Table I. For short growth times of graphene, the size of flakes is comparable on both substrates and exceeds 0.15  $\mu\text{m}$  for 350 s of growth. Also, the quantity of flakes increases with the increase of growth time up to 350 s. However, a further extension of time gives the opposite effect, i.e. the estimated size of flakes increases, while the quantity of flakes statistically decreases. Therefore, conclusions can be drawn that in case of Au/Cr/Al<sub>2</sub>O<sub>3</sub> the 1200 s is the threshold for graphene flakes forming and their size expansion, while for HR-GaN this phenomenon occurs faster, namely for 550 s.



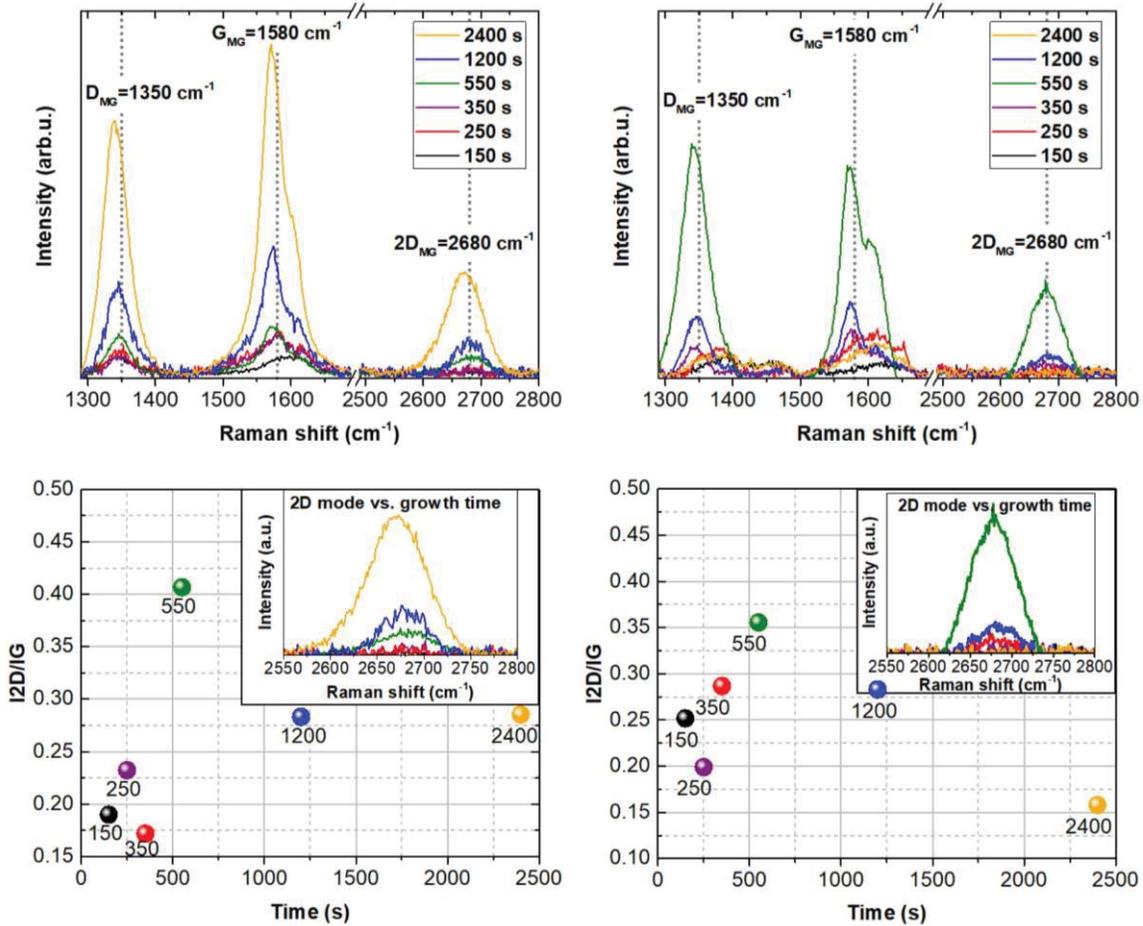
**FIGURE 1.** The top-view SEM micrographs of the Au/Cr/Al<sub>2</sub>O<sub>3</sub> (upper) and the HR-GaN (lower) time-dependent surface changes.

Raman laser with a spot size of 0.3  $\mu\text{m}$  was used to recognize the structural origin of observed bright-contrast flakes. Two distinct and high-intensity modes were detected and recognized as the defective D mode with a maximum at approx. 1350  $\text{cm}^{-1}$  and the G mode with a maximum at approx. 1580  $\text{cm}^{-1}$ . Hopefully, both substrates shared the presence of the 2D mode at the Raman shift of about 2700  $\text{cm}^{-1}$ , which corresponds to the hexagonal arrangement of carbon atoms in graphene.

**TABLE 1.** Quantitative analysis of the SEM micrographs as a function of growth time, obtained by computer image analysis. Presented results corresponds to average values.

Time growth [s]	Au/Cr/Al <sub>2</sub> O <sub>3</sub>		HR-GaN	
	d [μm]	quantity	d [μm]	quantity
150	-	-	0.13	54
350	-	-	0.15	15
550	0.53	91	0.52	15
1200	0.70	39	0.53	73
2400	0.55	115	-	-

The full width at half maximum (FWHM) value for 2D mode was about 73 cm<sup>-1</sup> for Au/Cr/Al<sub>2</sub>O<sub>3</sub>, while 2D FWHM for HR-GaN was 55 cm<sup>-1</sup>, which is more than in high-quality monolayer graphene (~30 cm<sup>-1</sup>) [14, 15]. Such wide FWHM value indicates three-layer graphene. Figure 2 compares the intensity ratios of 2D/G modes versus graphene growth time. As reported in the literature, the intensity 2D/G ratio for a high-quality graphene monolayer is 4:1 [16]. However, as the number of graphene layers increase, this ratio decreases below 1. Taking into account the high intensity of the defective D peak and comparison of these findings with those of literature studies we suggest that the bright-flakes are indeed carbon structure starting to organize into highly ordered graphene areas.

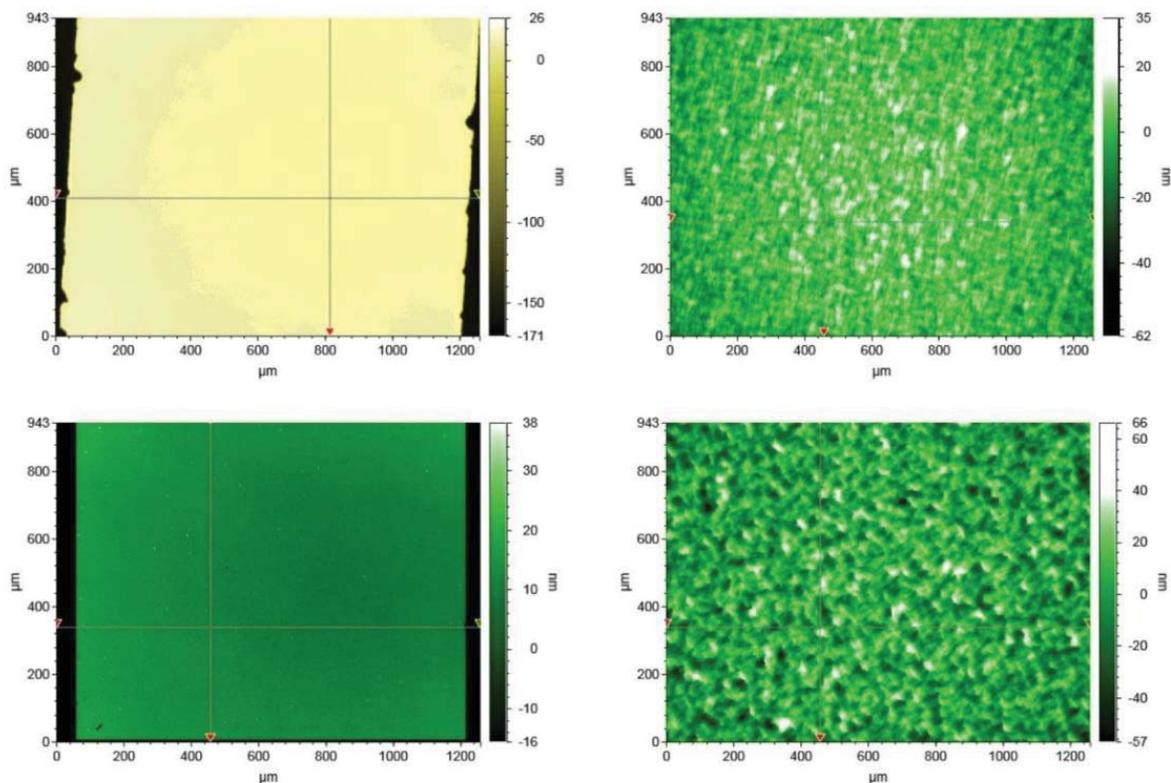


**FIGURE 2.** The raman spectroscopy: Raman spectra of graphene grown on Au/Cr/Al<sub>2</sub>O<sub>3</sub> (left column) and HR-GaN (right column) substrates at different growth times. At the time of 2400 s, The graphene-related 2D peak at 2680 cm<sup>-1</sup> can be clearly observed for Au/Al<sub>2</sub>O<sub>3</sub> and HR-GaN at 2400 s and 550 s, respectively. The lower part of the Figure corresponds to I<sub>2D</sub>/I<sub>G</sub> intensity ratio.

Before explaining these observations, it is necessary to know the surface condition of the studied samples, as well as the reference samples. To determine the surface roughness, the surface imaging, and the root-mean-square (RMS) parameter were measured by an optical profilometer. The results of these measurements are presented in Figure 3 and Table II. As can be seen, the surface roughness of reference HR-GaN was about 6.9 nm and was several times higher than the roughness of the reference Au/Cr/Al<sub>2</sub>O<sub>3</sub> (0.8 nm). The RMS value of HR-GaN results from the heteroepitaxial growth of GaN on the sapphire. This value is the consequence of the difference between the lattice constants of both materials. However, the measured RMS parameters for both substrates increased also after the PECVD growth of graphene, keeping the difference at a similar level. A possible explanation for the observed differences in the threshold growth times might be the different surface roughness of both substrates. As reported, the RMS parameter for HR-GaN substrate after 550 s growth was higher than for Au/Cr/Al<sub>2</sub>O<sub>3</sub> at 1200 s. This finding suggests that HR-GaN is more susceptible to the operation of PECVD growth conditions, leading to surface etching. A strong relationship between CVD growth conditions and GaN etching has been reported in the literature. Yun et al. reported that the H<sub>2</sub> etching of GaN surface allows to produce an active surface for graphene deposition through the exposure of Ga atoms [11]. Therefore, surface defects may be the privileged places for graphene growth. The analysis of the results of graphene growth on Au/Cr/Al<sub>2</sub>O<sub>3</sub> suggests that the observed longer time of graphene formation and expansion can be explained through the nobility of gold and the lack of catalytically active surface.

**TABLE 2.** The root-mean-square parameters for Au/Cr/Al<sub>2</sub>O<sub>3</sub> and HR-GaN substrates before and after graphene growth. The presented data are respond to 1200 s growth on Au/Cr/Al<sub>2</sub>O<sub>3</sub>, and 550 s growth on HR-GaN.

Sample	Au/Cr/Al <sub>2</sub> O <sub>3</sub> 1200 s [nm]	RMS HR-GaN 550 s [nm]
reference	0.8	6.9
PECVD growth	1.8	15.1



**FIGURE 3.** Surface topography of Au/Cr/Al<sub>2</sub>O<sub>3</sub> (left column) and HR-GaN (right column) mapped by the optical profilometer.

## CONCLUSION

This paper has discussed the possibility of obtaining a graphene layer on GaN and Au substrates using the plasma-enhanced chemical vapour deposition method. By applying methods of structural characterisation, we demonstrated that instead of the continuous graphene layer, the graphene in a form of spatial flakes have occurred. The research has also shown the impact of growth time, leading to the conclusions: the PECVD growth time affects the number and size of graphene flakes on HR-GaN and Au substrates. However, the optimum time for graphene growth on these substrates is different. Under presented conditions applying a growth time of about 1200 s is optimum for graphene growth on Au/Cr/Al<sub>2</sub>O<sub>3</sub>, while a shorter growth time of about 450-550 s is more beneficial for graphene growth on HR-GaN. Furthermore, the studies presented that the growth of graphene flakes is supported by the state of the surface, indicating that there are privileged places serving as catalysts for the growth.

The obtained flake-form of graphene excludes its application as transparent conductive electrodes for which a layer-form is required. However, our studies suggest that the PECVD could be a method for the synthesis of graphene flakes. Moreover, the obtained form of graphene may have potential in Au-based sensors, where the spatial form of graphene would increase the effective sensing surface. A considerably deeper study will need to be done to determine the impact of other PECVD parameters such as plasma voltage and power, pressure, and gas flow ratios. Also, further work is needed to fully understand the mechanism of graphene formation through the PECVD method in order to obtain a continuous graphene layers.

## ACKNOWLEDGMENTS

This work was supported by the Research Foundation Flanders (FWO) under Grant no. EOS 30467715.

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