

In situ kinetic studies of CVD graphene growth by reflection spectroscopy

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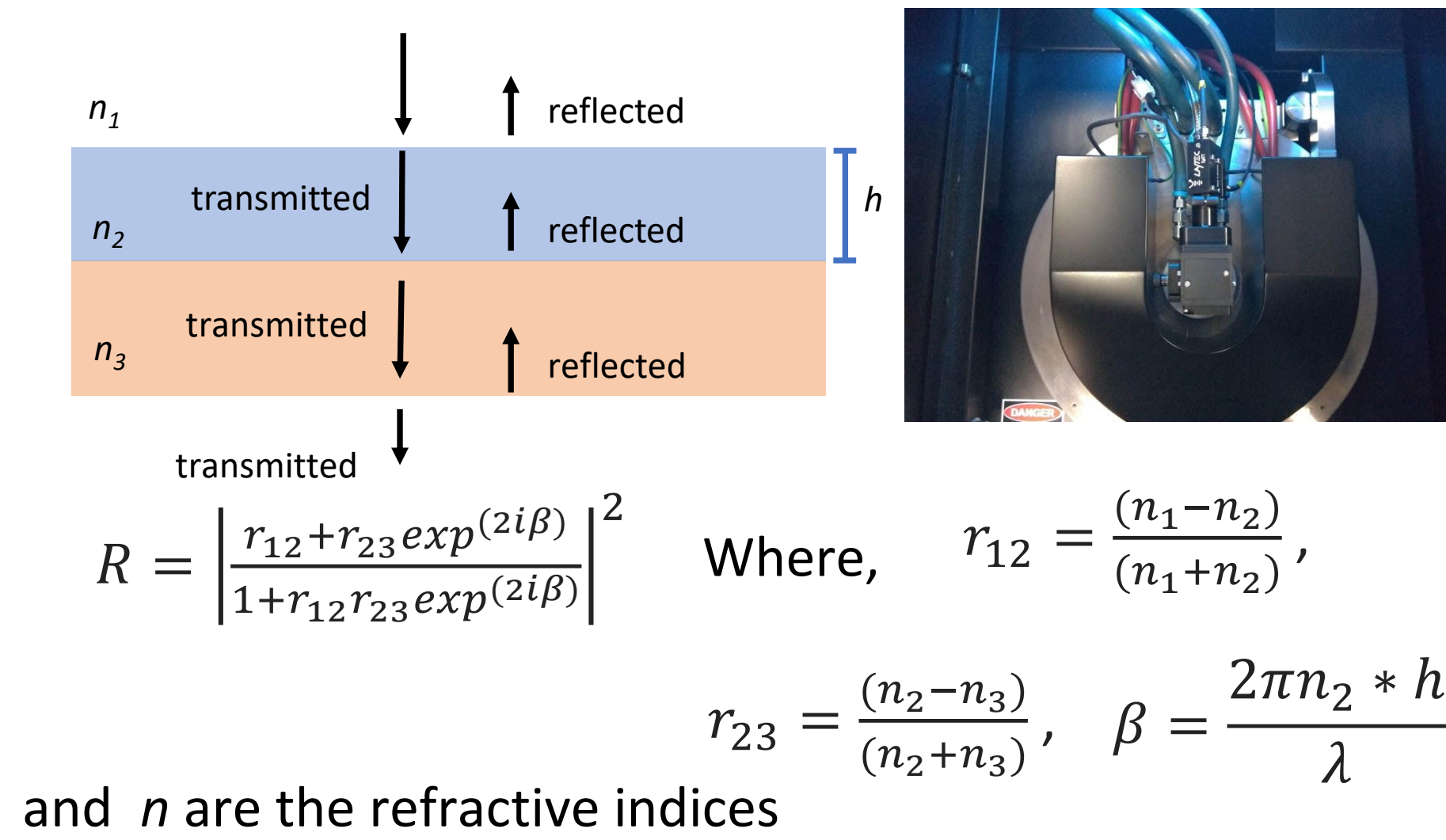
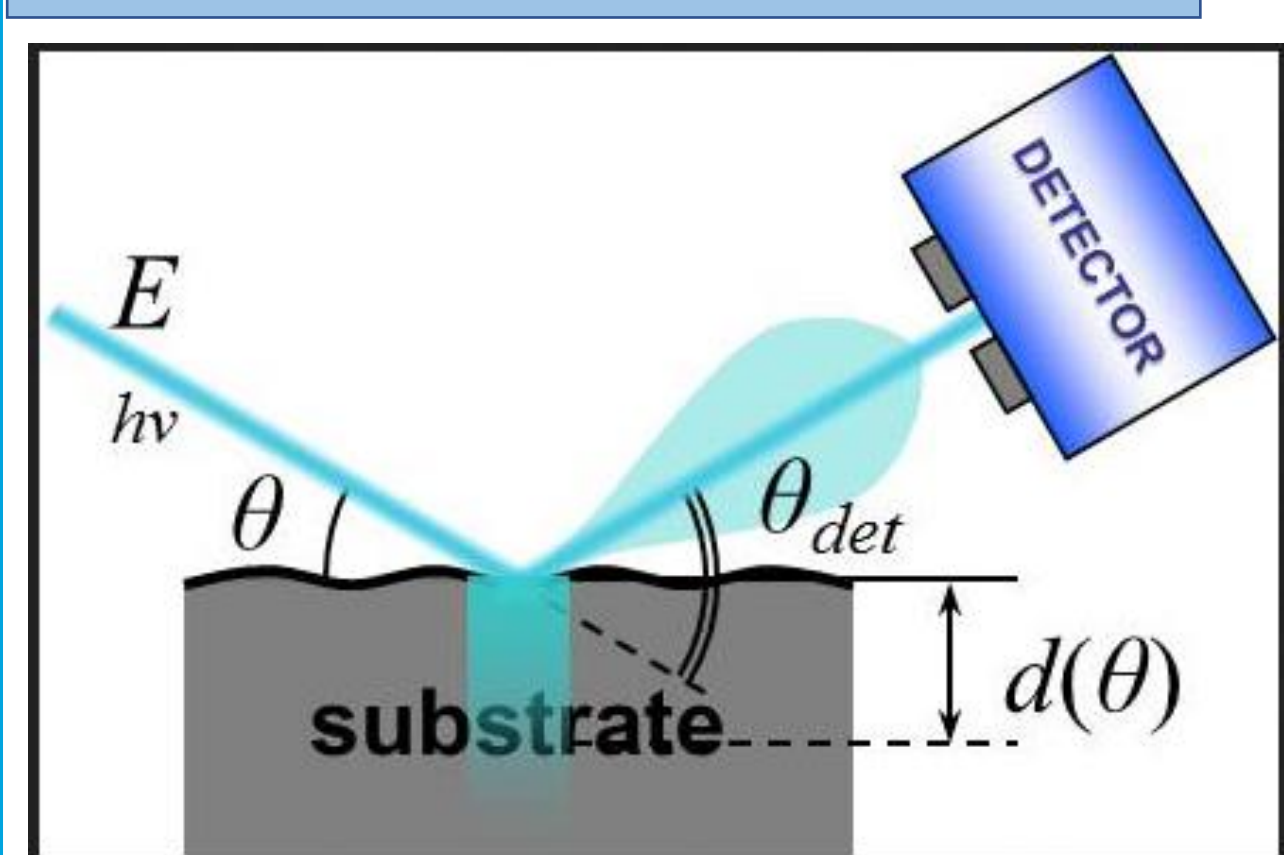
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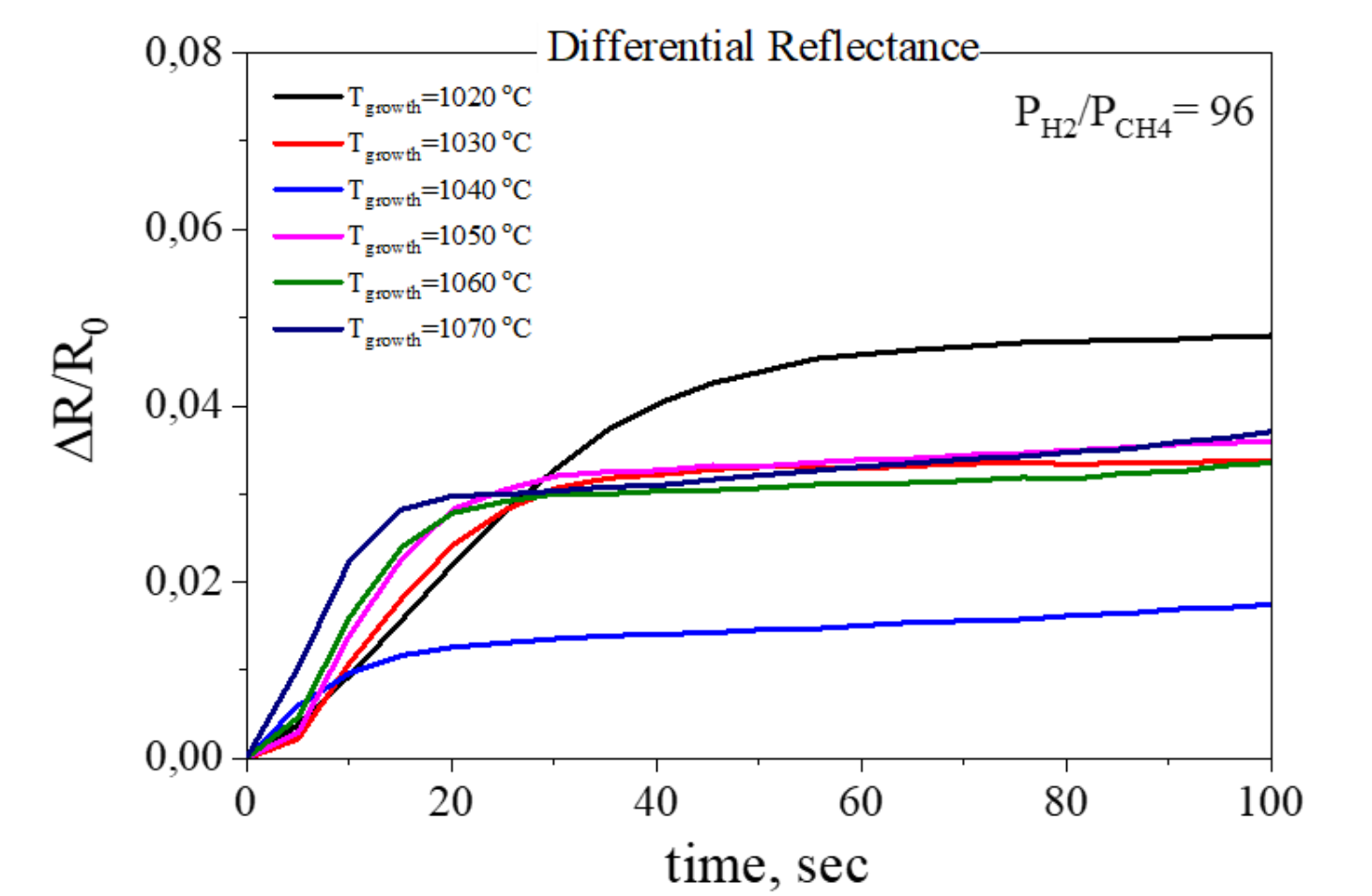
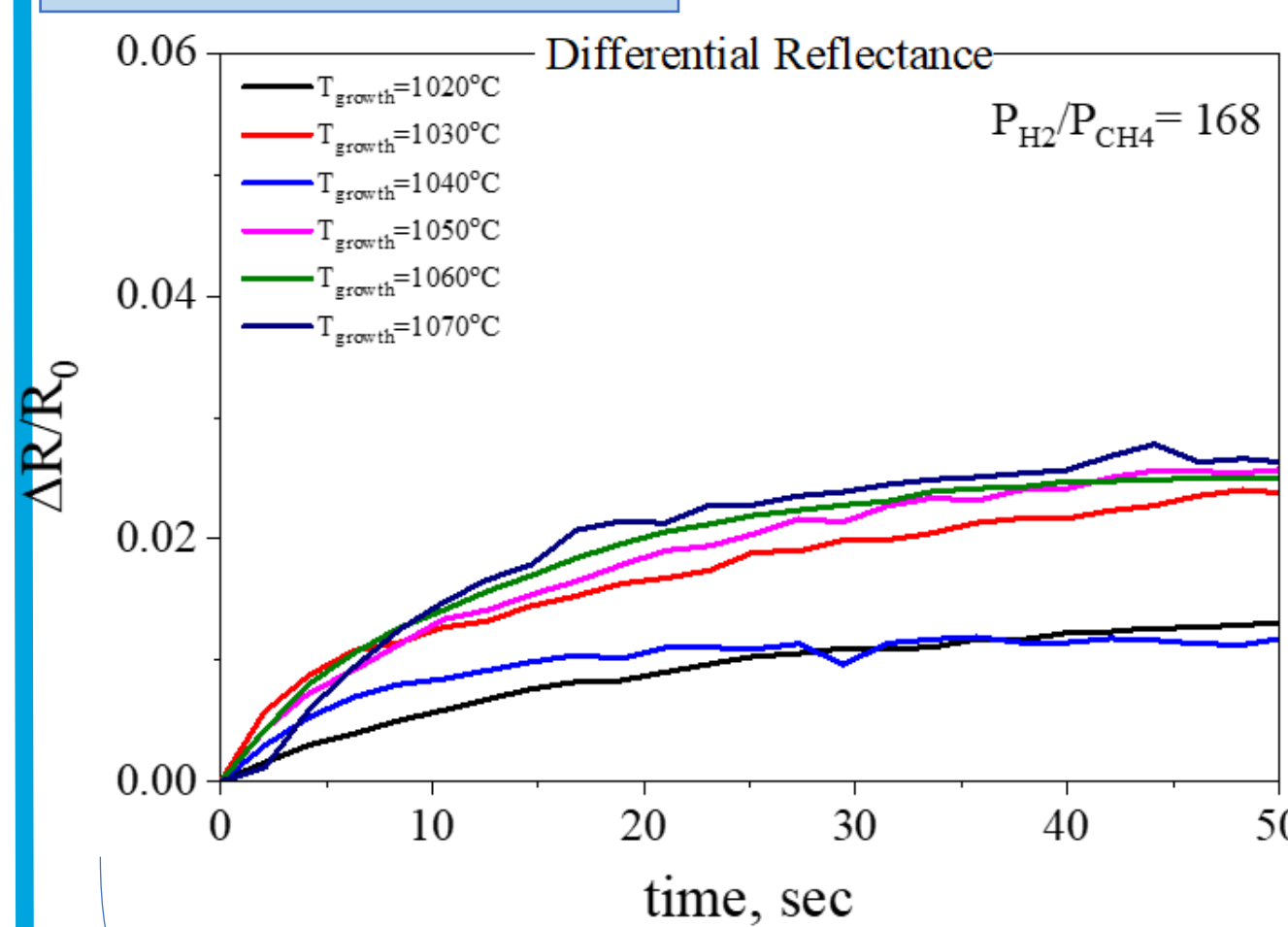
Introduction

Monitoring of large-scale synthesis of two-dimensional materials (2DMs) such as graphene is a prerequisite for industrial applications. Chemical vapor deposition (CVD) is currently the most widespread synthesis method as it is efficient and easy to automatize. The process itself is quite complex and poorly understood, but it is generally believed to involve a number of distinct steps such as hydrocarbon decomposition into surface-bound intermediates, diffusion on the catalytic substrate, generation of nucleation points and, finally, graphene growth. In situ monitoring and tailoring of such a complex procedure is beneficial for understanding the growth kinetics and, eventually, for controlling the graphene growth. Herein, we report on a novel metrology system based on in situ reflectance spectroscopy that has been developed for real-time monitoring of surface changes during graphene growth on Cu foils at high operating temperatures. The implementation of this technique for extracting kinetic parameters of the growth process is presented. Furthermore, a microkinetic model of graphene growth based on density-functional theory (DFT) and the hindered translator/rotator model for enthalpy and entropy corrections is constructed and used to obtain a microscopic understanding of the apparent activation energy and related rate-determining steps in graphene.

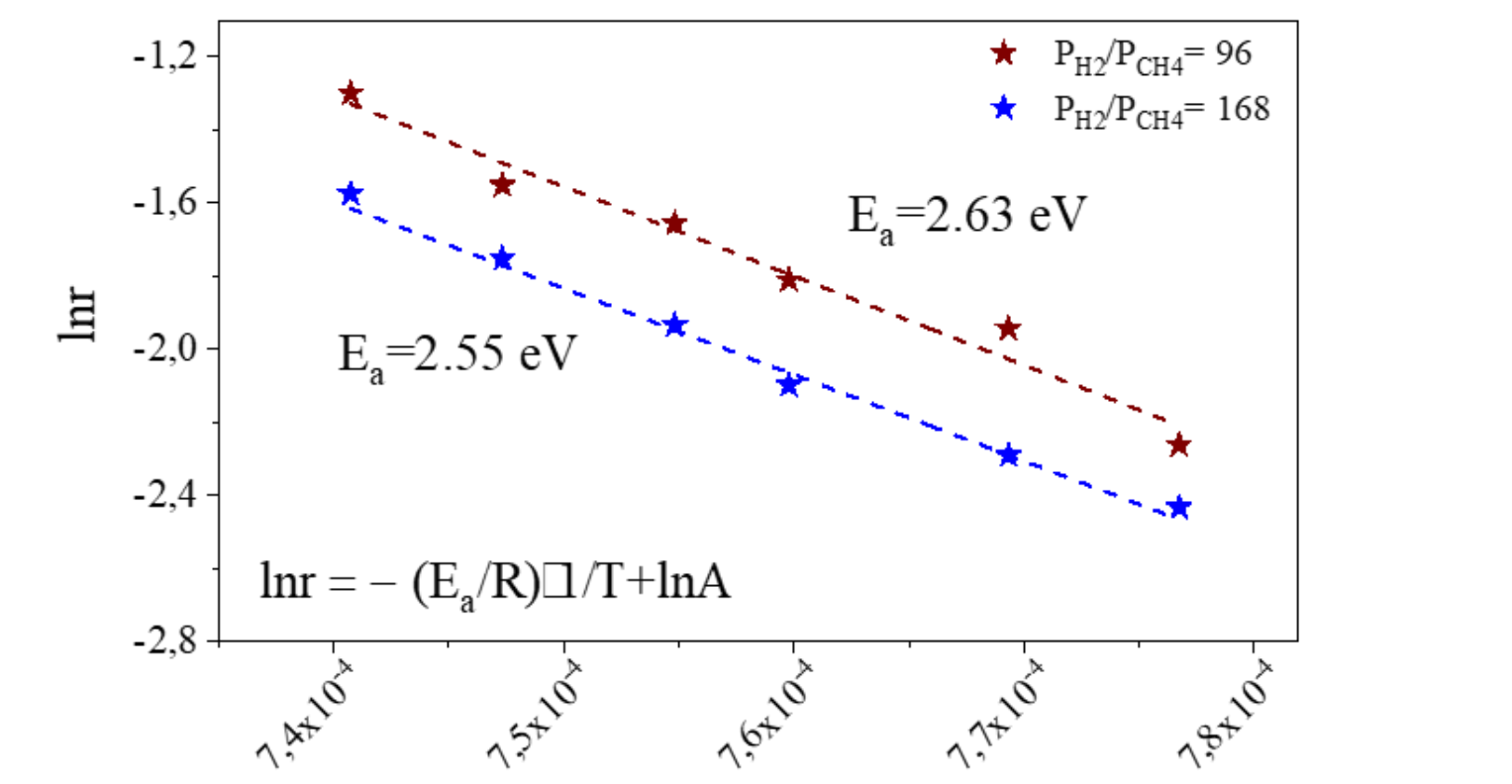
Working Principle



Growth kinetics



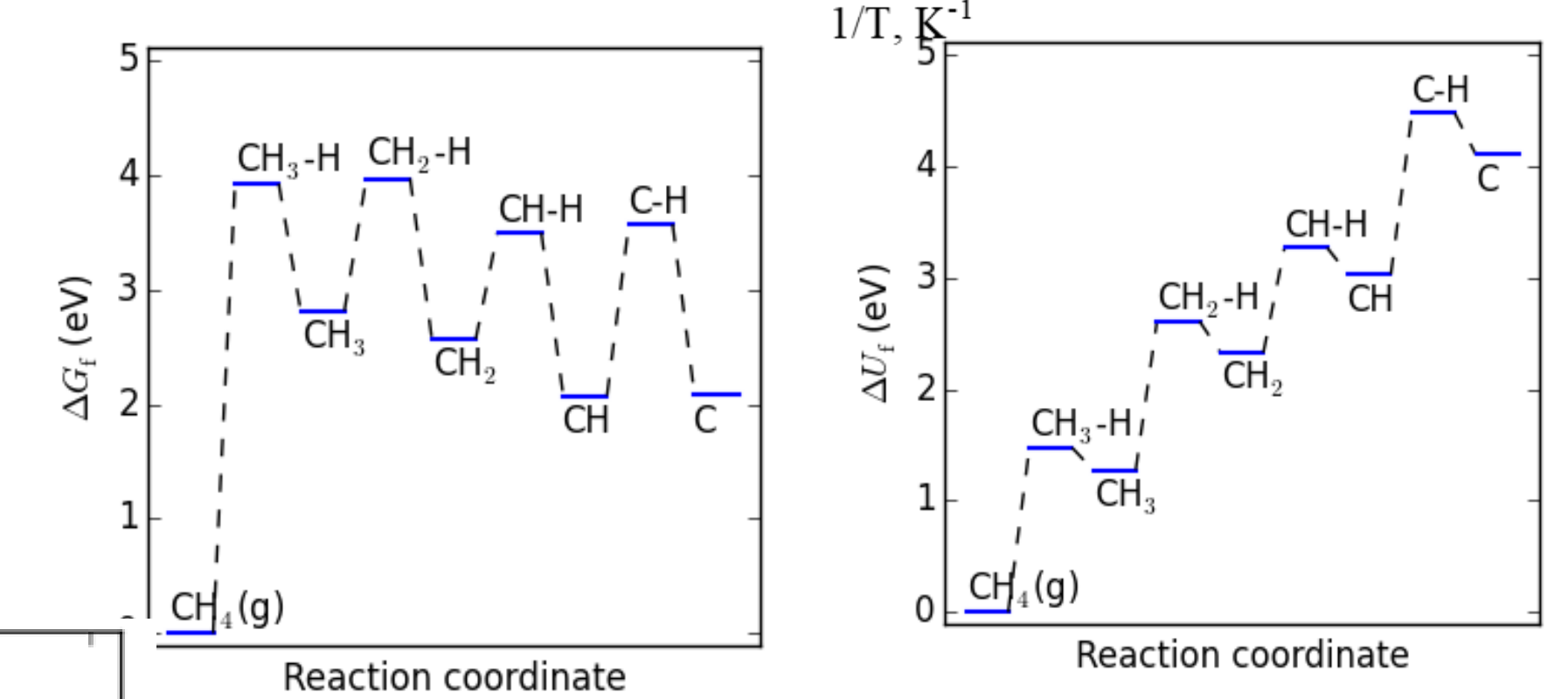
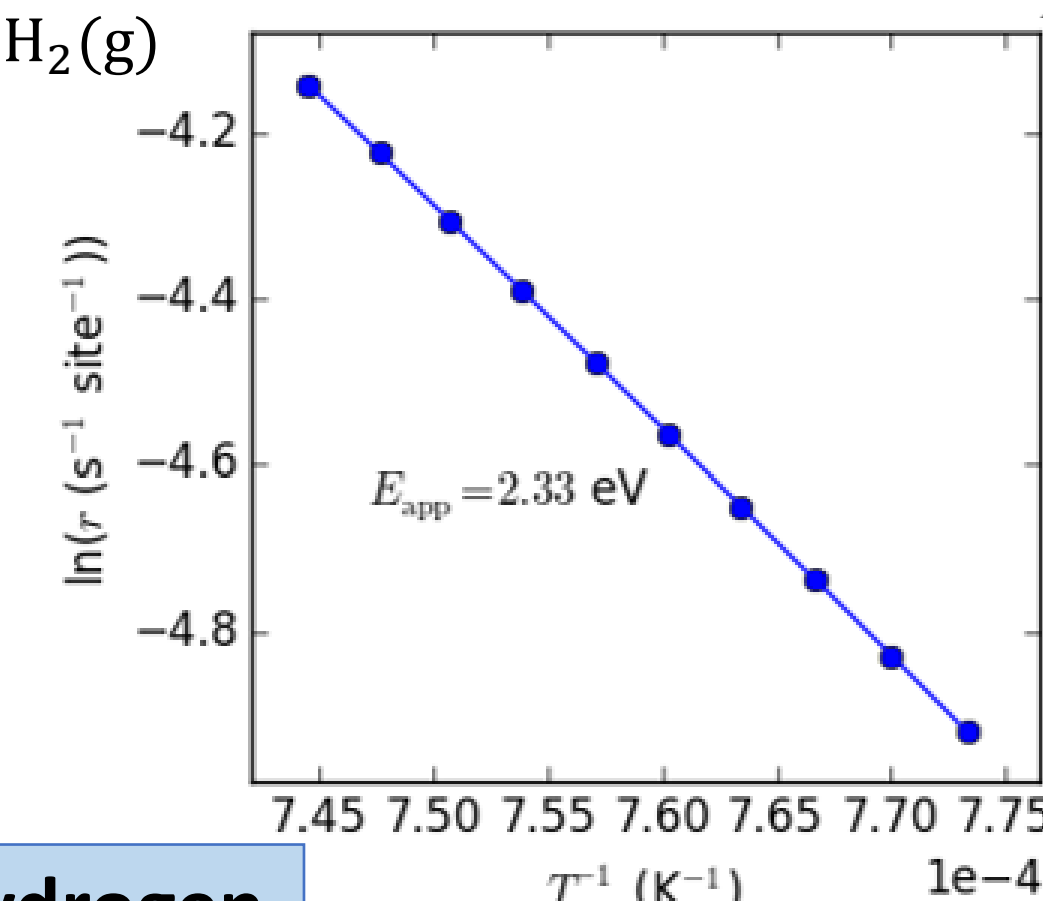
The growth rate was calculated by measuring the time it takes to reach the plateau of $\frac{\Delta R}{R}$ which corresponds to full coverage of the examined area with Graphene.



Microkinetic modelling

A simplified effective reaction scheme was proposed :

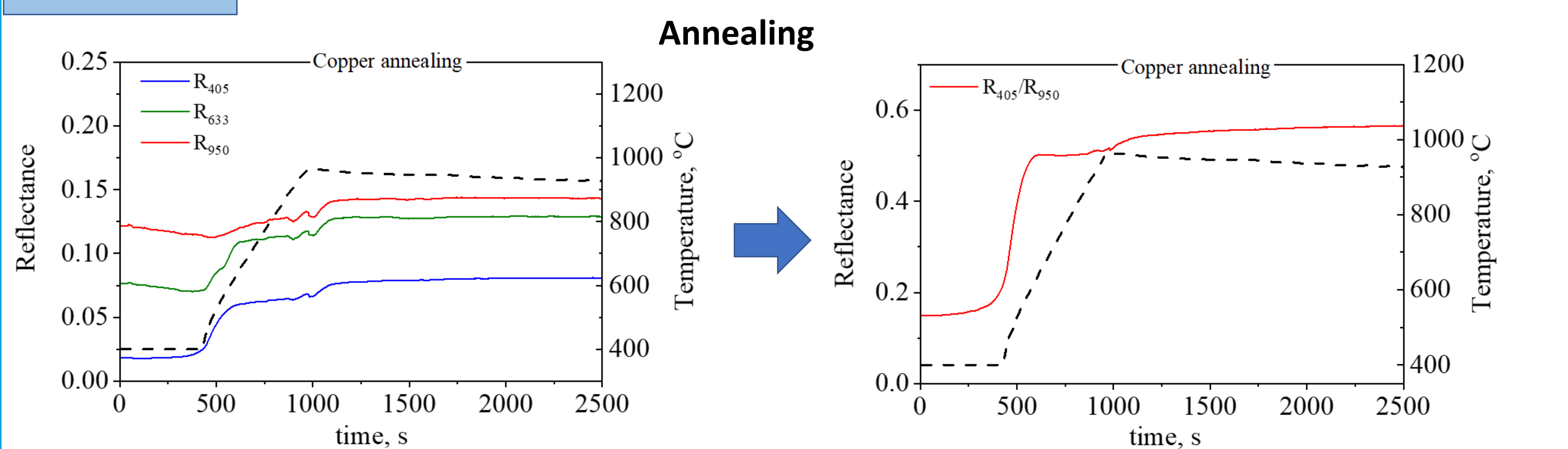
- $\text{CH}_4(\text{g}) \rightleftharpoons \text{CH}_3^* + \text{H}^*$
- $\text{CH}_3^* \rightleftharpoons \text{CH}_2^* + \text{H}^*$
- $\text{CH}_2^* \rightleftharpoons \text{CH}^* + \text{H}^*$
- $\text{CH}^* \rightleftharpoons \text{C}^* + \text{H}^*$
- $\text{C}^* \rightleftharpoons \text{C}(\text{g})$
- $2\text{H}^* \rightleftharpoons \text{H}_2(\text{g})$



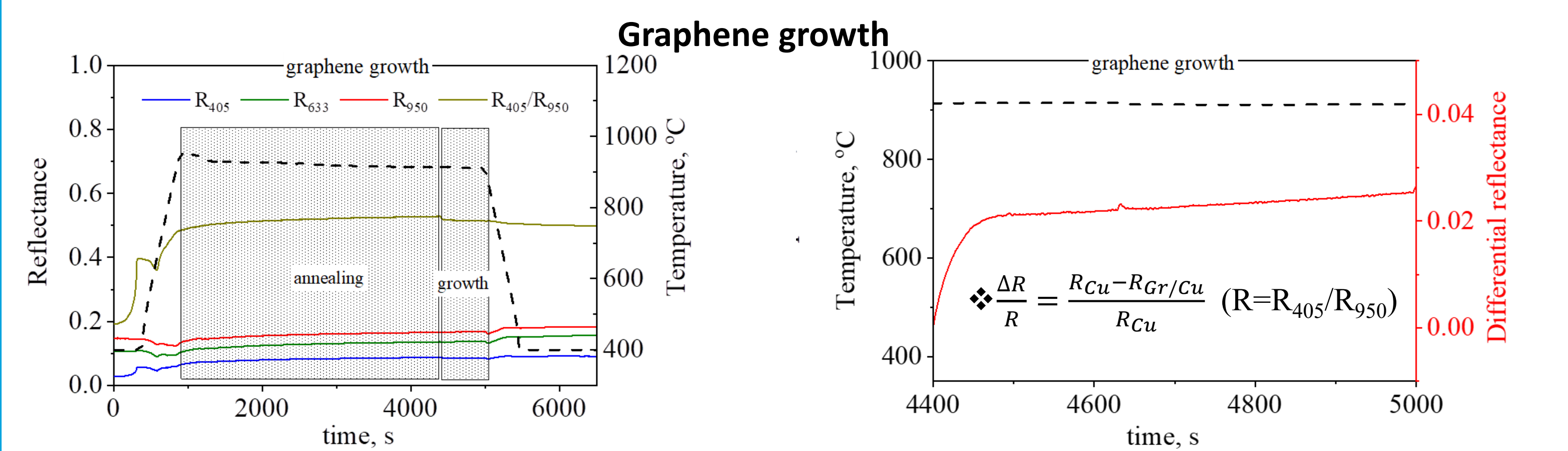
$$E_{app} = RT + \sum_i X_i \Delta U_{f,i} \text{ where } X_i = \left(\frac{\partial(\ln r)}{\partial(-\Delta G_{f,i}/RT)} \right)_{\Delta G_{f,j} \neq i}$$

Good agreement between the theoretical apparent activation energy E_{app} and the experimental value.

Results

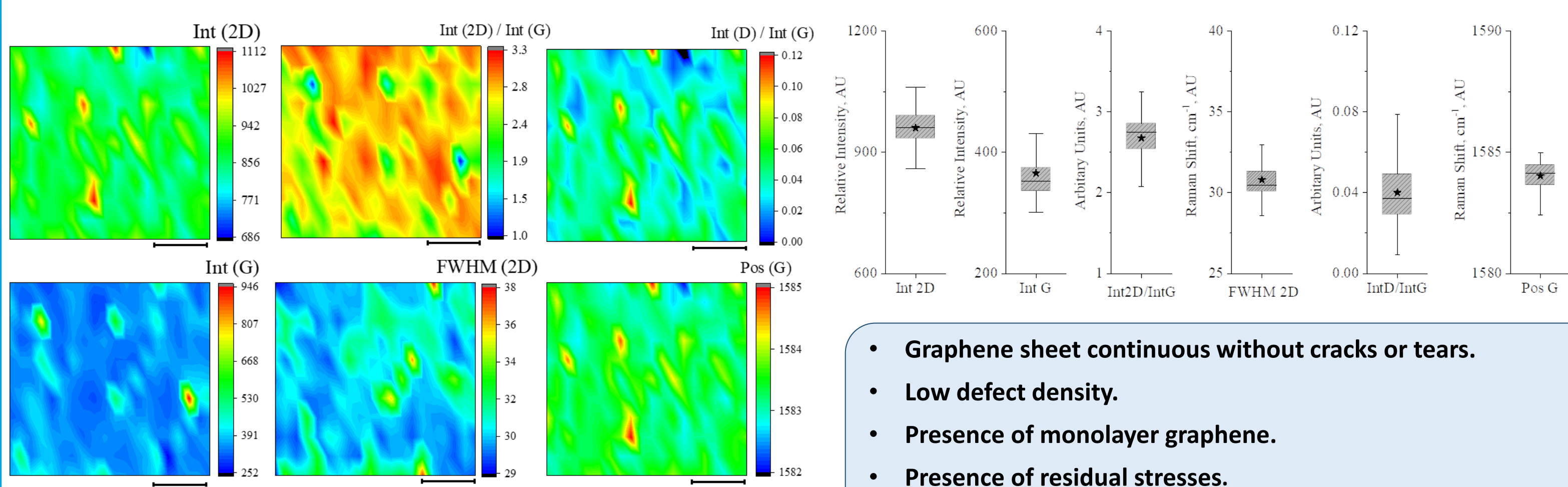


The R405/R950 was employed to exclude the variation of the reflectance caused by morphological changes.

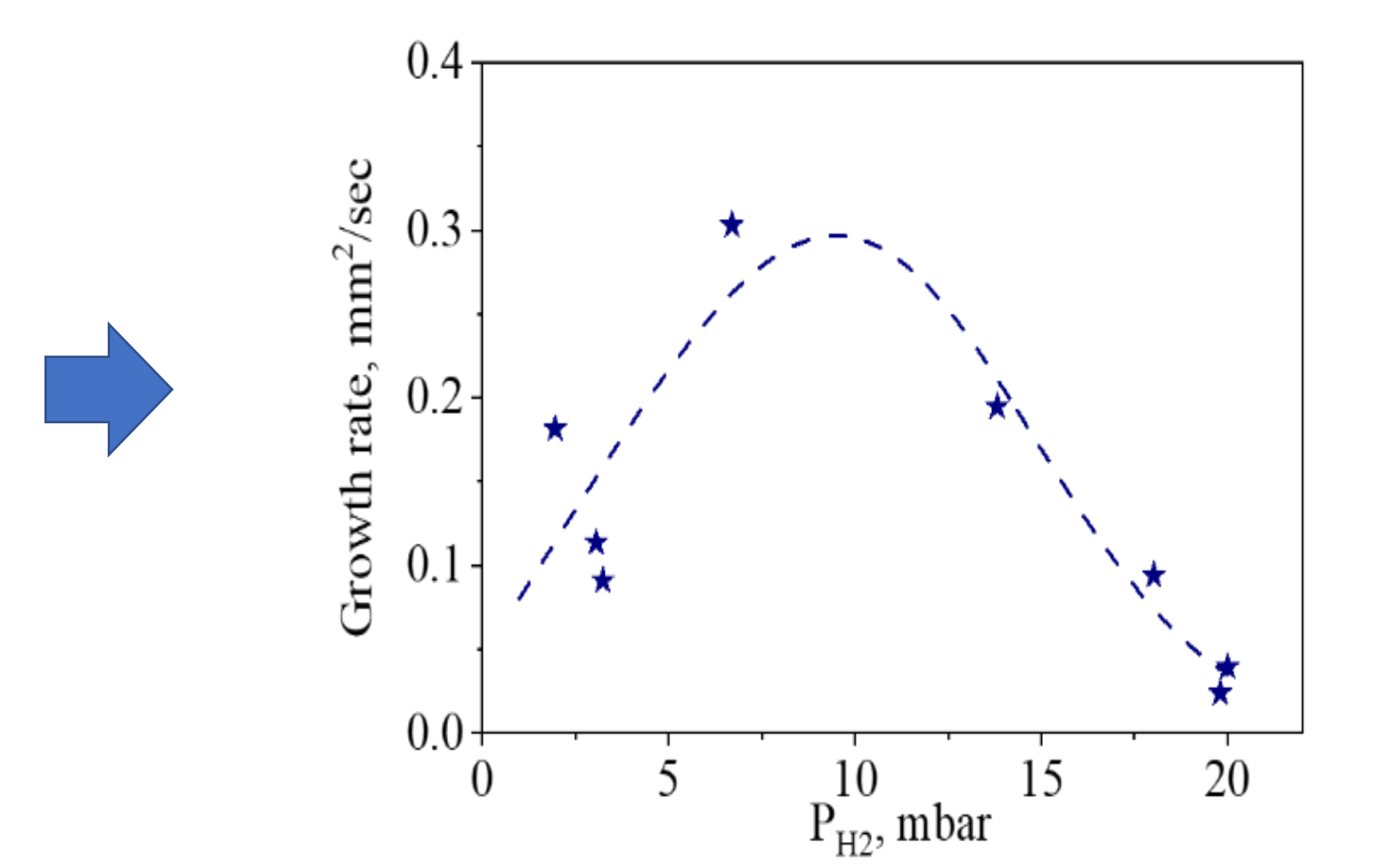
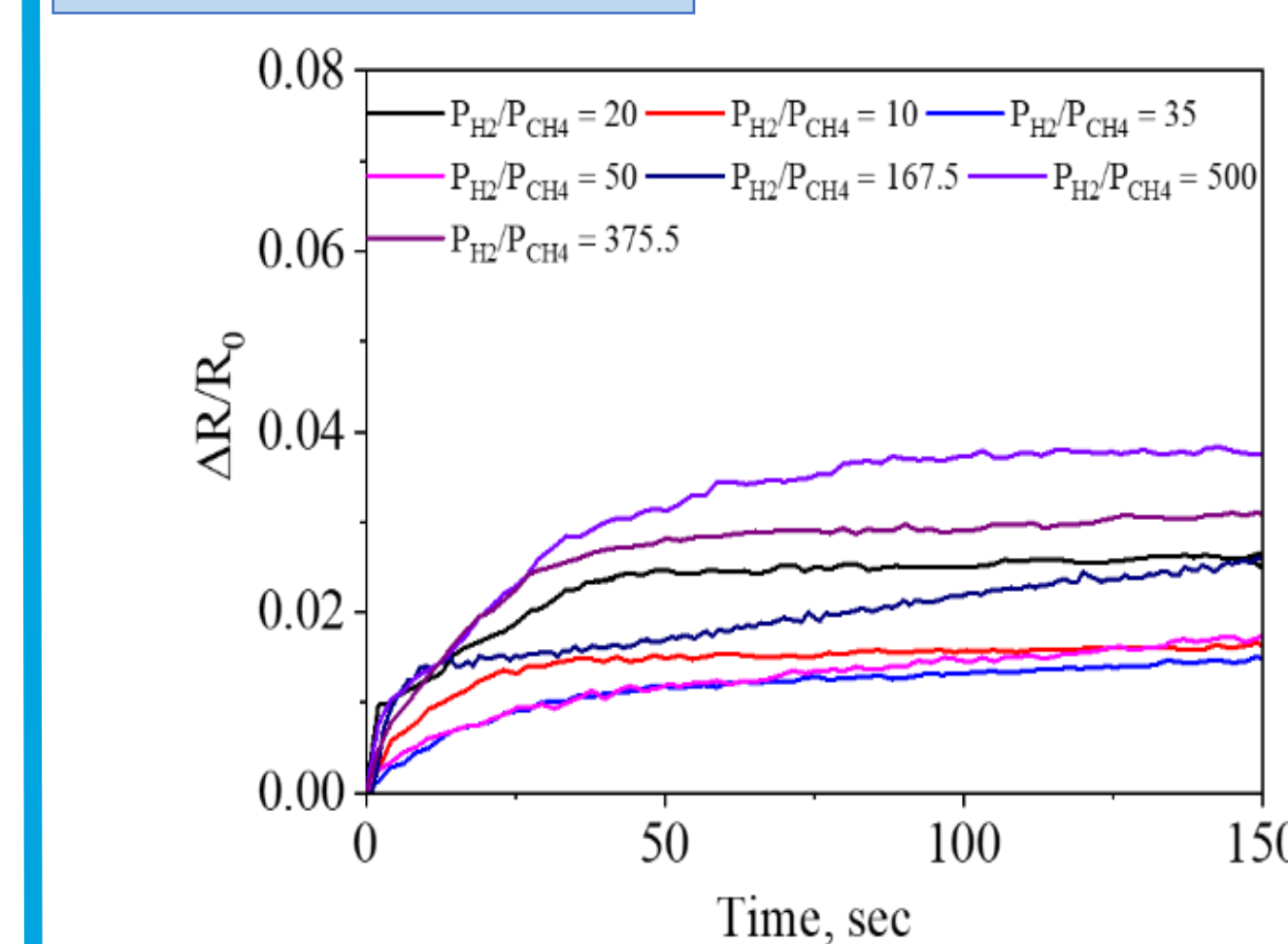


The quality of the graphene and the number of graphene layers can be investigated via differential reflectance.

Quality control with Raman spectroscopy



Role of hydrogen



Low partial pressure of Hydrogen improves the catalytic activity of the Cu surface.
High partial pressure of Hydrogen acts as an etching reagent.

Conclusions

- The differential reflectance spectroscopy is a vital tool for in situ characterization and monitoring of the growth.
- Good agreement with both the experimental apparent activation energy and the overall growth rate. This implies that the subsequent diffusion and growth steps are likely not rate-determining.
- The first two dissociation steps (i.e. the steps from $\text{CH}_4(\text{g})$ to surface-bound CH_2^*) are both partly rate-limiting.
- The hydrogen plays a rather complex role in the CVD process, i.e. it acts as a catalyst activator at low hydrogen contents and as an etching reagent at high hydrogen contents.

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REFERENCES

- C. Tsakonas, M. Dimitropoulos, A.C. Manikas, C. Galiotis, *Nanoscale* 13 (2021) 3346-3373.
- C. Tsakonas, A.C. Manikas, M. Andersen, M. Dimitropoulos, K. Reuter, C. Galiotis, *Chemical Engineering Journal*, 421 (2021) 129434.
- T. Kaplas, A. Zolotukhin, Y. Svirko, *Opt. Express* 19 (2011) 17226-17231.
- Z. Mao, C.T. Campbell, *ACS Catalysis* 9 (2019) 9465-9473.