In-situ metrology for graphene growth

Promising results were achieved during first in-situ measurements with a multi-wavelength reflectometer during graphene growth on copper/silicon (Cu/Si) in an AIXTRON BM Pro 6-inch reactor. Although the surface changes during the process are rather complex, they can be analyzed using in-situ reflectance data. Here we present a tentative analysis of these first measurements.

1. Introduction

For several years, graphene has been the subject of intense research activity aimed at exploiting its unique properties. Unbreakable and foldable touch screens for mobile phones, faster computer chips, batteries of higher capacity – these are just a few of graphene's applications.

In this application note we report on recent results regarding in-situ monitoring of graphene growth on Cu/Si in a commercial AIXTRON BM Pro reactor [1]. We applied single wavelength reflectance at 405 nm for sensing the surface throughout the CVD run.

2. Experimental

The growth conditions in the AIXTRON BM Pro reactor have been as follows: precursor for growth on thin-film copper/silicon dioxide/silicon - methane; carrier gases - hydrogen and argon. The graphene was grown at 25 mbar with a gas mixture containing about 1% methane. Hydrogen was not used during the methane step.

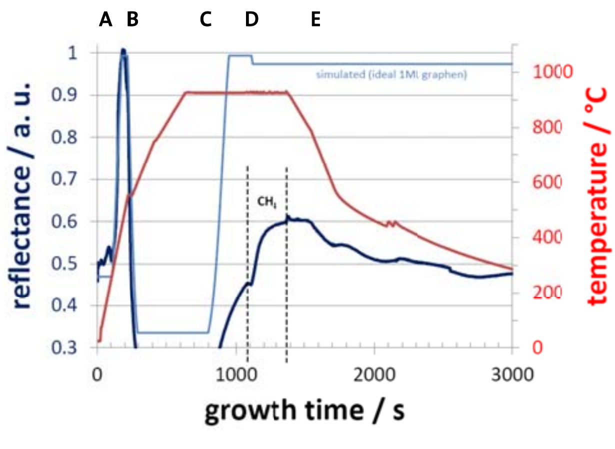

Fig. 1: CVD of graphene on Cu/Si in an AIXTRON BM reactor. Dark blue line - 405 nm reflectance measured in-situ during the growth; red line - the process temperature measured with a thermocouple; light blue line - the calculated 405 nm reflectance.

We applied a prototype 405 nm reflectometer measuring normal incidence reflectance through the standard optical viewport of the reactor. A time-resolved reflectance transient, as typically measured, is given in Fig. 1. The related reactor temperature has been added for reference. The capital letters A … E indicate the characteristic growth steps: copper oxide reduction (A), copper surface roughening (B), copper surface re-smoothing (C), graphene deposition (D), and cooling-down of the completed structure (E).

3. Tentative analysis

By using the published n and k optical data for graphene [2] and copper [3], we simulated the measured 405 nm reflectance response (see Fig. 1). The rapid increase in reflectance (A) at about 450°C is caused by the reduction of hydrogen induced oxide from copper. The rather large reflectance increase is consistent with the oxide thickness of 7 nm. Immediately after oxide desorption, the reflectance drops close to zero (B) probably due to copper sublimation in the temperature range between 600°C - 900°C. At higher temperature and especially during the high temperature annealing, the Cu surface becomes smooth because of the high mobility of Cu atoms on the surface (C). Our simulation of the characteristic reflectance response in (B) and (C) is simplified and does not yet account for the complexity of the morphological and structural changes that the layer experiences during the process. Further analysis is needed for a quantitative comparison with the experimental data. During CH_4 flow (D), the graphene film grows. According to our simulations (light blue line in Fig. 1) based on the optical n,k-data from [2], the growth of a graphene layer on a completely smooth Cu surface would reduce the 405 nm reflection by 1-2%. In the experimental data (Fig. 1, step D), however, the 405 nm reflectance increases during CH_4 flow. Our

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tentative explanation is that, due to further surface smoothing during this process step, the surface reflectance increases overcompensating any possible reflectance reduction due to graphene growth. Interestingly, the 405 nm reflectance decreases after the temperature is reduced below 800°C (E). The reason for this effect is still under investigation.

To test our assumptions on oxide reduction and to separate the effect of temperature and oxide removal, a growth run with different conditions for de-oxidation was performed. It was proved that the initial reflectance peak was, indeed, caused by the presence of copper oxide (see step A in both Fig. 1 and Fig. 2). In Fig. 2, the higher reflectance value at the end of step C shows that an extended high-temperature annealing produces a smoother Cu surface. This supports the hypothesis that not the graphene growth but the surface morphology changes are responsible for the reflectance rise in Fig. 1 (step C and D).

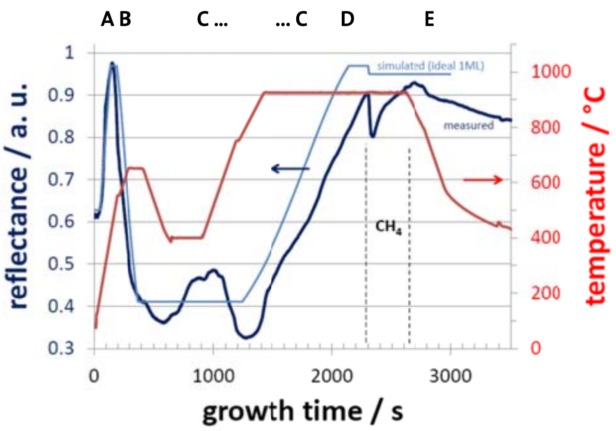

Fig. 2: CVD of graphene on Cu/Si in an AIXTRON BM reactor: run #2 with extended Cu annealing (C...C). The simulated reflectance (light blue) with intermediate surface roughening (step B), surface re-smoothing (step C) and one layer of graphene deposited (step D) is added for reference.

The reflectance level reached during the second run, just before the start of the CH_4 step, is nearly as high as the peak measured during the oxide desorption. Then, an evident reduction in 405 nm reflection due to graphene deposition under CH_4 is seen (D). This effect, however, is much too large to be explained by the deposition of a single graphene monolayer. Ex-situ microscopy on this sample revealed some pinholes in the Cu that were attributed to high-reflectance silicon substrate being visible. Obviously, the Cu surface undergoes some complex structural and morphologic transformation, including Cu atom desorption, that cannot be simply described as roughening/re-smoothing. Therefore, the large reflectance response under CH_4 in Fig. 2 is most probably not simply correlated to the graphene growth: it could be a Fabry-Perot signature due to the underlying SiO_2 layer showing up through the vanishing Cu. Alternatively, the changeover of gas species in the reactor or slight change in thermals in the reactor and on the surface of the wafer could also contribute to the reflectance change. Our tentative conclusion is that a longer anneal on a slightly thicker Cu layer would lead to an improved surface morphology for the deposition substrate.

4. Conclusion

This preliminary study clearly demonstrates the sensitivity of the 405 nm reflectance to surface processes like de-oxidation and roughening during graphene CVD on Cu. In case of growth on Cu/Si, the combination of temperature, low pressure and CH_4 supply does change the surface properties of the copper substrate and causes copper removal from the surface. Therefore, a sensor able to monitor in-situ both surface temperature and 405 nm reflectance, like LayTec's EpiTT, can deliver valuable information to understand and optimize the deposition process.

Further systematic in-situ studies by academic customers will give new insights into the physics and chemistry of such processes, and complement the results of other, more complicated techniques as spectroscopic ellipsometry in [2]. For future large-scale production reactors, where ellipsometry ports usually cannot be easily integrated, either normal incidence 3-wavelength reflectance (EpiTT) or even UV/visible spectroscopic reflectance (EpiR DA TT) could serve as efficient in-situ metrology tools both for R&D and future process control.

Acknowledgement

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For further information and consultation please contact info@laytec.de or visit www.laytec.de

[1] AIXTRON BM datasheet
[2] M. Losurdo *et al.*, J. Phys. Chem. C 2011, 115, 21804ff.
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