Mechanical behaviour under thermal loading of metallic thin films used as catalysts for graphene growth under CVD

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Abstract - As boundaries in the miniaturization of technology are being pushed to smaller lengths, nanotechnology and in particular 2D materials such as graphene have been subject of considerable recent attention. The preferred technique for its production is chemical vapour deposition (CVD), using a copper thin film as a catalyst for growth. Attempts have been made to lower the film's thickness to reduce material costs, but this causes the film to become unstable at higher temperatures, which in turn inhibits graphene growth. It is thought that the stresses the film is under during the process can be a source for unstable behaviour.

A model using the finite element method was developed using the software Abaqus both in 2D and 3D, where films of different thicknesses would undergo a thermal cycle simulating that of the CVD process, so as to study the mechanical behaviour of the thin film during that process.

The results showed that stress levels remained similar for all film thicknesses. Residual plastic strain is usually low in the cases studied (≈ 0,2%), but there is the possibility that this cannot be neglected, as far as graphene film growth is concerned. A comparison with molybdenum showed that the behaviours of the two materials were similar, especially when the concept of homologous temperature is introduced. The results of the 3D analysis confirmed the findings of the bidimensional study.

Keywords: Thermal loading, thin films, graphene growth, finite element method

I - Introduction

In recent times, we've seen a quest from tech companies to push the boundaries of the capacity of the devices we carry in our hands while at the same time shrinking their size so that they don't exceed the palm of our hands. This has led manufacturers to turn to new alternative materials that allow them to continue this trend and give them the performance they need.

One of such materials is graphene, who is to withstand vey high temperatures, as well as being stronger than steel and a better conductor than copper[1], which make it very suitable for applications in electronics and fibers.

The main process used for graphene synthesis is chemical vapour deposition (CVD), which consists in a catalyst-assisted decomposition of hydrocarbons through high temperatures, between 600°C and 1200°C, allowing the material to grow atop the catalyst material in the reactor[2]. In this reaction, the graphene growth starts at the defects and impurities of the substrate and grows into islands by adsorbing the carbon at the interface with the substrate to expand its surface area. For this process copper is a preferred substrate as it is inexpensive, easily soluble and has low carbon solubility, meaning that carbon elements stay at the surface during CVD and allow graphene islands to grow.

The problem of copper is that the CVD process requires temperatures that are close to its melting point and this causes instabilities, like the dewetting of the film, that prevent graphene growth. One way to ensure that the film stays stable is to increase its thickness[3], but thinner films would be advantageous in a mass production scenario.

In Thompson's overview of the dewetting process[4], he explains how the film becomes unstable and eventually become

unsuited for graphene growth purposes. This process consists in the formation of "islands" of agglomerated material as thin films are heated up to high temperatures. The formation of these islands usually starts at pinholes at the boundaries between grains, with triple boundaries being a weak point, where capillary energies will drive the hole growth until the surface reaches a stable state. These capillary energies cause a flux of material away from the edge of the hole, causing the hole to grow. As this process continues to occur at different pinholes in the film, its surface becomes compromised and the result is the island-like topography that is associated with dewetted films.

Aside from the instabilities, stresses can also hamper the graphene growth process due to the possibility of affecting the surface of the copper thin film and its adherence to the substrate below[5]. Two aspects were considered relevant: the intrinsic stresses developed during the deposition of the film on the substrate and the thermal stresses it is subjected to during the CVD process.

For the first, it results from when the thin film is sputtered on top of a substrate, a consequence of the atomic arrangement under conditions far from thermodynamic equilibrium, whereby the growing film is subjected to atomic and ionic bombardment from the gas phase. This occurs during deposition and does not include explicitly thermal stresses. As the material is deposited, islands are formed under stress due to the interface shear stresses between film and substrate, a consequence of lattice mismatch and atomic and ion bombardments[6]. The continued deposition of material allows for island growth until they coalesce and form a film. At the end of the deposition, two scenarios are possible: in the case of materials with high-mobility atoms they diffuse from the edges of grains and relax stresses, while in the case of materials with low-atomic mobility stresses stay at the same level as there is no diffusion from the grain edges to cause relief.

The second stress source is thermal stress. This comes from the difference in thermal expansion coefficient between the film and the substrate at a given temperature. This differential causes biaxial stresses that can cause the film to buckle or peel from the substrate, depending on the stresses applied [7].

II - Methodology

In order to be able to study the stress-strain state of the thin film during the CVD process, we turned to the Abaqus software to recreate this situation with a virtual model. The finite element method on which Abaqus is based uses difference equations to solve partial differential equations that simulate real world conditions. To do this, the model converts mathematical equations into matrix models that can be approximated through nodes and elements that are appropriate for a computer to solve[8].

The model is based on the typical structure of substrate and catalyst thin film described previously for the CVD process and they undergo a thermal cycle to simulate the stresses that arise during this process. The substrate is made of two layers, a thicker one made from silicon and a silicon dioxide layer on top of it. Two materials were chosen for the simulation of the thin metallic film, copper and molybdenum. To compare how they behave under high temperatures and temperature gradients during the process. Four different thicknesses of the thin film were modelled, 900nm, 480nm, 120nm and 30nm to see how they would influence the process. As a way to minimize the need for computational power, the thickness of the silicon was reduced from 800μm to 10μm. A representation of the layout of the measurements can be seen in Fig 2.1.
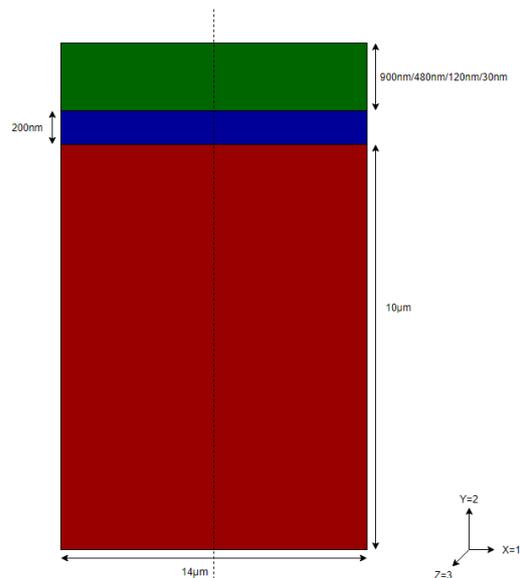

Fig 2.1 – *Schematic of the bidimensional model*

A three-dimensional model was also developed to verify the results observed in the bidimensional studies. The three-dimensional

models consist of a 480nm or 120nm thin copper film, with lengths varying between 5μm, 10μm, 20μm and 40μm.

In order to implement the plastic behaviour of the two thin film materials, the yield and ultimate stresses for the very high temperatures that they would be subjected to were needed. As they were not available, some of the values had to be extrapolated using Arrhenius' law. The substrate materials, silicon and silicon dioxide were treated as purely elastic.

For the bidimensional models, the simulation consisted of a heating phase from room temperature up to 250ºC, 500ºC, 750ºC or 900ºC, followed by a cooling phase from peak temperature to room temperature. As viscoplastic and stress relaxation effects are not considered in these models, the time of each phase is not relevant, and as such each phase had the duration of 1 second.

As for boundary conditions, the bidimensional models were pinned along the bottom edge, and a symmetry condition was established across the X-axis to save on computing power. For the three-dimensional models, the boundary conditions of the bidimensional model were kept and a second symmetry condition along the Z-axis was added to further save on computational power.

With the finite element method, a convergence study is performed to evaluate the consistency of the results as the number of elements in the model increases. In this case, since the geometry of our models is very simple, there were no problems with the convergence of the results already from a very low element count. For the bidimensional models, a goal was set to maintain an element density that would ensure the existence of at least 5 elements along the thickness of each layer. However, maintaining this rule and an identical element size in the whole model would mean that the 10μm thick layer of silicon would have a drastic impact in the computational resources needed as the number of elements in that layer would be very high. As such a biased seeding approach was adopted for the silicon layer with elements becoming taller as they are farther away from the silicon dioxide layer, allowing to maintain a reasonable overall element count while ensuring that the top layers were at least 5 elements thick. When transitioning to a three-dimensional approach, the number of elements

also varies with the difference in length of the model. Since it was decided to keep the 5 element thick layers it meant each layer needed to have differently sized elements, with different thicknesses while keeping the width and the length equal.

Finally, it was assumed that all the materials were isotropic, that there were no initial stresses in the film, and all the bidimensional studies were realised under plane strain conditions.

III – Results

Starting in the thicker 900nm copper film, the results indicated that stress levels increased as the temperature rose until the yield stress value was met, at which point they gradually lowered until the end of the heating phase. As the cooling phase began stress levels started rise again and kept increasing until the film reached room temperature again (Fig 3.1).
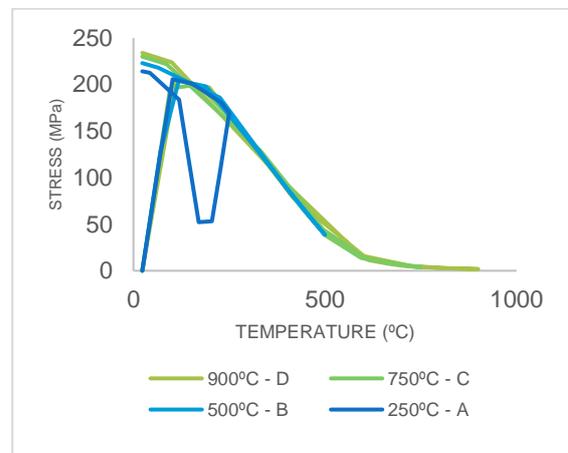

Fig 3.1 – *von Mises stress at the centre of a 900nm copper film*

A closer look showed that stress levels were more intense at the centre than at the extremity of the thin film. We also learned that stress levels were much higher in the S11 and S33 main stress components, along the X-axis and Z-axis, at the centre, while at the extremity stresses were mainly represented by the S33 component. The S22 and S12 stresses remained low in both points. The evolution of copper's yield stress with temperature also

proved to be an interesting comparison with the von Mises stress results (Fig 3.2) as they were closely matched for the higher peak temperature cycles. For the lowest peak temperature cycle of 250ºC we could also notice that there was a period at the start of the cooling phase where stress levels dropped, signalling a return to elastic deformation that was visible in the plastic strain results. This was characterised by a plateau that starting as the cooling phase began before plastic strain values started to drop off as the film reached room temperature.
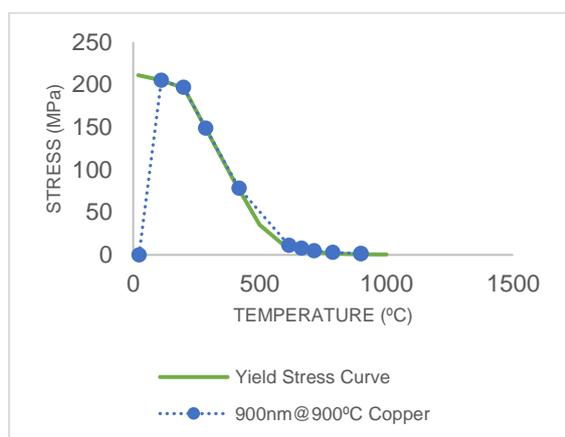

Fig 3.2 – Evolution of yield stress with temperature and comparison with von Mises stress from 900nm copper film

Lowering the film's thickness yielded similar results, with stress levels remaining very close to what we observed in the thicker film with the same distribution. Although it was minimal, we would like to note that the S22 stresses, along the Y-axis, rose as the film's thickness lowered at the extremity but not at the centre.

As an alternative to copper, the preferred metal used during the CVD process, we also performed the same analysis with a molybdenum film. Molybdenum was chosen due to its higher fusion temperature which makes it more stable at temperature levels required for the process.

The results showed that there were similar trends in both materials, but stress levels were higher in the molybdenum films (Fig 3.3). While the mismatch between the thermal expansion coefficients of the substrate and the thin film, which causes thermal strain, is not as severe in the case of a molybdenum film when compared to a copper film, the molybdenum's

higher Young's modulus causes stress levels to rise above those of the copper film. One difference between the two was in the plastic strain results, where for lower peak temperature cycles the plateaus did not drop off as the film cooled down.
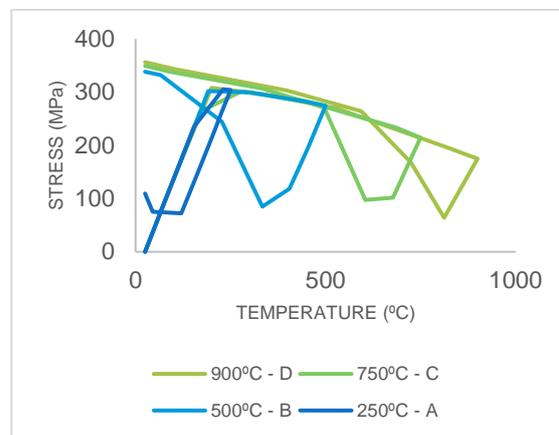

Fig 3.3 - von Mises stress at the centre for a 900nm molybdenum film

As there were similar trends in both materials, like the drop in stress values at the start of the cooling phase and the plateaus in the plastic strain results, but that occurred at different points in the cycle, we resorted to the homologous temperature to try to find a point of comparison between the two materials. The homologous temperature measure temperature as a fraction of the fusion temperature of the material. We attempted to find the point at which the dips in stress and the plastic strain plateaus stopped appearing in both materials and see if the homologous temperature at that point matched.

We observed that the dips in stress disappeared at a similar homologous temperature, but the same was not the case for the plastic strain plateaus. A comparison between the evolution of the yield stress curves with homologous temperature of both materials (Fig 3.4) show that at the point where the stress dips stopped occurring, the curves were very close which suggests a relation this behaviour and the state of the thin film.
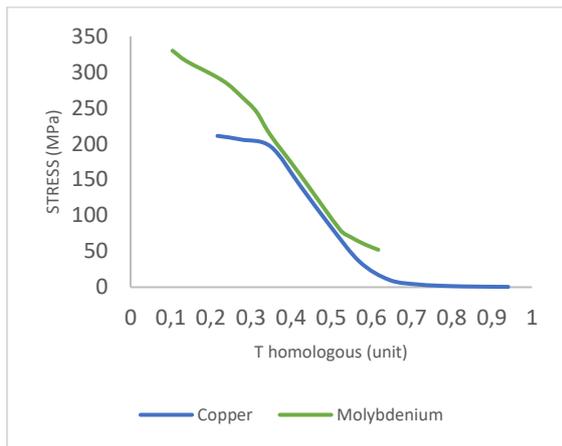
Fig 3.4 - *Evolution of yield stress with homologous temperature in copper and molybdenum*

As we move to a three-dimensional model, we shifted our focus from the thickness of the thin metal film to its length. Starting with the 480nm thick copper film, we saw that in the 250ºC peak temperature cycle stress levels were comparable in all different four different thicknesses, but there were differences during the beginning of both heating and cooling phases, as longer films tended to have higher stress levels than shorter films (Fig 3.5)
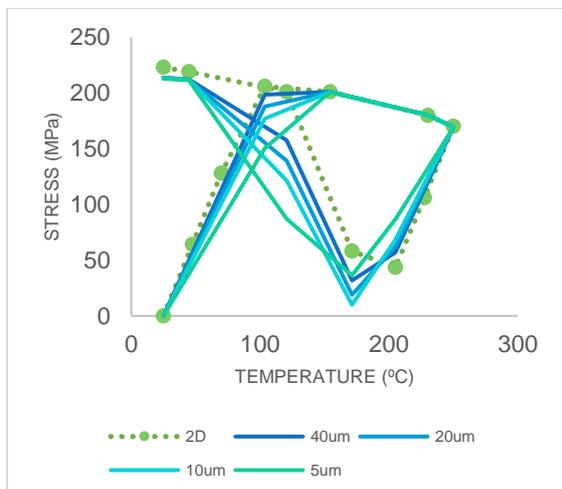

Fig 3.5 - *von Mises stress at the centre of a 480nm copper film, 3D model*

Stress levels and behaviours were similar to what was reported from the bidimensional model. Stress distribution is also reminiscing of the bidimensional model, with higher stress levels at the centre for S11 and S33 components. The plastic strain results mirrored that of the von Mises stress as we observed that shorter films started to deform later and with shallower curves, which in the case of the 5µm long film also meant that plastic strain levels were lower.

Increasing the peak temperature to 500ºC showed the impact of the evolution of the yield stress with temperature as the differences that were clear for a 250ºC peak temperature cycle were no longer there (Fig 3.5).
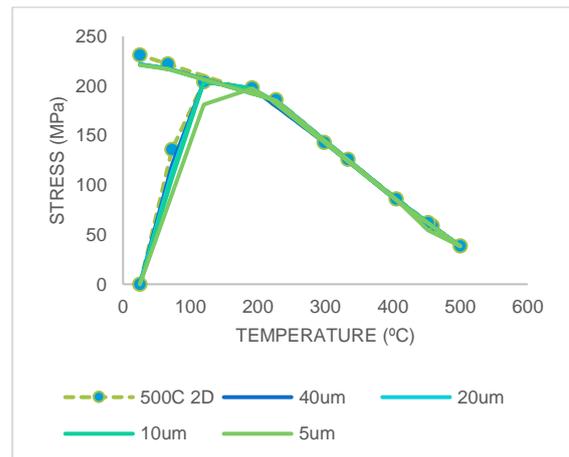

Fig 3.6 - *von Mises stress at the centre of a 900nm copper film, 3D model*

We also performed the same simulations for a thinner 120nm copper film and had similar results to those of the 480nm film. However, in the cycle that peaked at 250ºC the stress and plastic strain results for the different lengths were not as spread as what was observed for the 480nm. The increase in temperature did nonetheless homogenize the results as was the case in the 480nm film.

IV – Conclusions

Although this model is very limited as it applies to a very specific case both in terms of geometry and starting conditions, it does provide a valid insight in how the film behaved. While the von Mises stresses were similar at both the centre and the extremity of the film, the two points were in fact affected by different stresses, as stress levels were lower at the extremity than at the centre. It was also found that the evolution of the yield stress as the temperatures increased conditioned the stress levels as the thermal cycle advanced, and how it homogenized them as we observed when we transitioned to a three-dimensional model.

The residual stresses for both copper and molybdenum films remained approximately constant regardless of thickness variations. The residual plastic strain was also constant for both materials and relatively low, however it is not negligible as it can have an impact of the film to serve as a catalyst for graphene growth since plastic deformation is associated with the presence of crystalline defects.

The comparison between the copper and the molybdenum films also showcased other interesting behaviours, in particular the fact that the two materials' stress curves trends were similar at the same homologous temperatures but the strain curves were not, suggesting that after a certain point in the temperature range there is a transition period common to both materials. The difference in the stress levels that we observed was also interesting as although the difference in thermal expansion coefficients was lower for the molybdenum films, stress levels were in fact higher due to its higher Young's Modulus compared to the copper. It was also observed that the copper films remained mostly in a plastic deformation regime while the molybdenum films deformed under plastic and elastic regimes.

As the model transitioned to a three-dimensional analysis, the results remained consistent. The study of the impact of length variation in the three-dimensional models did show that there was a coherence between the two approaches, as the results observed always converged towards what was reported for the 2D models as the assembly increased in size. This indicates that bidimensional models can be used to study the influence of process parameters on the behaviour of graphene catalysts.

However, many of the limiting factors of the metallic thin films used as catalysts in this process have not been taken into account in this model, such as the dewetting of the film due to instabilities at high temperatures, the initial stresses that emerge during the deposition of the thin metallic film on top of the Si/SiO_2 substrate and the stress relaxation effects that appear during the thermal cycle that were covered in this work. These are other avenues to further continue the study of the behaviour of metallic thin films during the CVD process.

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