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Time Dependent Structural Analysis of CVD Grown MoS_2 Flakes with Different Configurations

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Abstract

The relationship between the formation of long-term fractures in monolayer MoS_2 flakes and the chosen CVD growth approach is demonstrated. The CVD method comprises either face-down (FD) or horizontal (H) growth approaches where the FD method is frequently used due to the possibility of growing rather larger flakes. However, time dependent observation of these flakes suggests that the flakes grown by FD method is spontaneously fractured. On the other hand, flakes grown by H approach remains intact and crack-free (for this research, this duration is limited by a period of 18 months). Spontaneous cracking of the FD grown flakes is attributed to the stress accumulation during the presumably faster CVD growth. In plane Raman mode shifts of the cracked and transferred flakes supports the stress accumulation during FD CVD growth. These results are critical to understand and predict about the crack-free growth of 2-D materials for their devices to become commercialized in the future.

1. Introduction

2-D transition metal dichalcogenide semiconductors such as monolayer or few-layer MoS_2 present a high potential for flexible, transparent, and high-performance future electronic devices [1]. Bandgap transition from indirect (bulk) to direct bandgap (monolayer) and valley selective polarization constitute the main interest towards the research and integration process of these materials especially into optoelectronics field [2-3]. For these materials to be integrated into practical devices, long-term device stability is critical, which would require large scale and high quality films that could be functional for a sufficiently long period of time. In the case of large-scale homogeneous growth, absence of self-limiting growth mechanism is the main challenge [4]. However, although growth mechanism is not fully perceived, large scale film and/or flake growth is achieved to some extend by various methods including cost effective CVD setups and more complicated MOCVD systems [4]. Although there are several reports underlining a cracking and aging problem of these structures, which is attributed to the residual thermal strain effect [5-7], still the reliability of such monolayers in terms of long term mechanical integrity is not thoroughly studied yet. Thus, understanding and solving this problem is currently one of the utmost important issues. Therefore, in this work, time dependent fracture (or aging) comparison of the MoS_2 flakes grown by face-down and horizontal approach is demonstrated. CVD growth conditions such as growth time, precursor amounts and temperature are kept constant. More importantly heating and cooling rates are kept identical for both configuration. A clear difference is found on the mechanical stability of the flakes grown by face-down and horizontal approaches, where the face-down flakes spontaneously crack but horizontal flakes are kept as grown even it exceeds 18 months after their growth.

2. Experimental Procedure

Schematic representation of the face-down and horizontal CVD growth is demonstrated in Fig. 1. In FD growth, Si/SiO_2 substrates are positioned on top of the MoO_3 precursor and in H growth substrates are positioned next to the precursor. 1 mg MoO_3 and 150 mg Sulphur are reacted for 10 minutes at 700 °C to form MoS_2 flakes in a quartz tube at an atmospheric pressure. 400 sccm N_2 is used for both oxidation protection and as carrier gas.

The flakes are characterized by measuring μ-Raman and photoluminescence spectra. Transfer of the substrates is achieved by the wet transfer method. Time dependent fracture behavior of the flakes are observed by dark field optical and confocal microscopy.

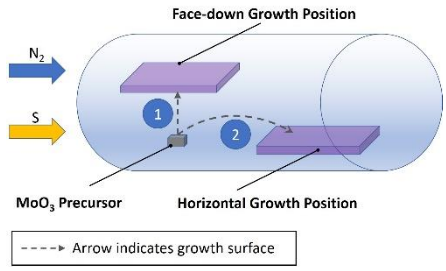

Fig 1. Schematic view of CVD growth of FD and H positions. Arrow 1 and 2 indicates the surface where MoS_2 flakes grow. S indicates Sulphur.

3. Results & Discussion

Fig. 2 represents the freshly grown flakes by using the two approaches. PL peaks are centered at 1.8 eV for both of the samples. As noted before, the flakes of the face-down sample (Fig. 2a) are larger than the horizontally grown ones (Fig. 2b). Considering the 10-minute identical growth time, growth rate of the FD flakes are much higher than the H flakes.

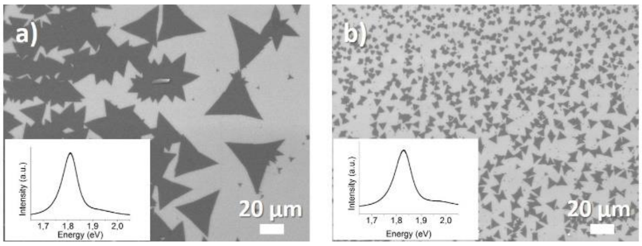

Fig 2. SEM images of freshly grown a) FD flakes and b) H flakes. Insets demonstrate 1.82 eV PL bandgap indicating monolayer MoS_2.

Fig. 3.a represents the confocal optical image of FD cracked sample, where centers of the flakes are fractured. Fig. 3.b is the dark field optical image of the same flakes indicating new edges created after the fracture of the flake. Fig. 3.c shows confocal image of a transferred FD flake on a new substrate. Fig. 4.d demonstrates E^1_{2g} and A_{1g} Raman signatures of the flakes.

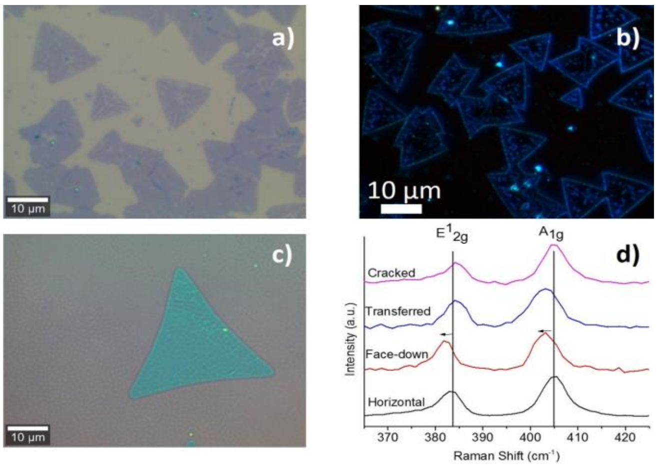

Fig 3. a) Cracked FD flakes, b) dark field image of cracked flakes, c) confocal optical image of transferred FD flakes, d) Raman signatures of the cracked FD, transferred, freshly grown FD and H flakes. Arrow indicates a blue shift of the Raman modes of face-down sample.

Uniaxial strain studies on MoS_2 have clearly demonstrated that in-plane E^1_{2g} vibrational mode blue shifts when tensile stress is applied [8]. In Fig.3.d, it is clear that Raman modes of the face-down sample blue-shifts with respect to H grown samples indicating a tensile stress inside the FD flakes. When these flakes are transferred on a new surface, this stress relaxes and Raman modes red shifts to their relaxed positions and overlaps with Raman modes of the horizontal case (Fig 3.d, transferred sample). Interestingly, when the Raman modes of the cracked face-down flakes are investigated, the same red shift is observed with the transferred flakes. This result indicates that the stress is relieved with the fracturing of the flakes. Also, it is observed that the face-down approach provides a tensile stress inside the flakes comparatively higher than the horizontal growth. In other words, stress remained in samples grown by horizontal approach does not cause any cracking effect.

There is a striking thermal expansion difference between monolayer MoS_2 (10^{-5}/°C) and the SiO_2 ($5.6x10^{-8}$/°C) [7]. It is suggested that the high growth rate together with this high thermal expansion difference in FD growth cause rather a high stress in the films and/or flakes. This rather higher growth rate in FD configuration is asserted not only due the larger flake size (Fig 2. a and b). but also, due to the much higher amount of vapor phase radicals (Mo and S). In the case of horizontal growth, considerable amount of radicals are lost by diffusion in the chamber.

4. Conclusions

In conclusion, two different growth approaches are compared by observing the change in their flake structures in time (for 18 months). It is demonstrated that face-down growth approach yields larger flakes with a significant stress accumulation that leads to spontaneous cracking of the FD flakes. On the other hand, horizontal growth approach yields smaller but mechanically stable flakes that is at least stable for more than one and half year.

Acknowledgements

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