High-performance transistors based on monolayer CVD MoS$_2$ grown on molten glass

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Transition metal dichalcogenides (TMDCs) are emerging two-dimensional materials for their potential in next-generation electronics. One of the big challenges is to realize a large single-crystal TMDCs film with high mobility, which is critical for channel materials. Herein, we report an optimized atmospheric pressure chemical vapor deposition method for growing large single-crystal monolayer MoS$_2$ on molten glass substrate with domain size up to 563 $\mu$m. Better interface quality can be achieved using high-{$\kappa$} dielectrics with respect to the conventional thermal SiO$_2$. Mobility up to 24 cm$^2$/V·s at room temperature and 84 cm$^2$/V·s at 20 K can be obtained. This low-cost growth of high-quality, large single-crystal size of two dimensional materials provides a pathway for high-performance two dimensional electronic devices. Published by AIP Publishing.

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Transition metal dichalcogenides (TMDCs) have attracted enormous research attention for electronic and optoelectronic applications due to their excellent transport properties and ultrathin body nature.\textsuperscript{1–4} Compared with zero bandgap graphene\textsuperscript{5–7} and black phosphorus,\textsuperscript{8–10} TMDCs contain a rich family of various materials with versatile electronic properties.\textsuperscript{11} Extensive work has been done on CVD growth and charge transport of monolayer MoS$_2$ in recent years. The atomically thin thickness, low dielectric constants, heavy carrier effective mass, and large bandgap of MoS$_2$ can greatly suppress the short channel effects below $\sim$5-nm gate lengths.\textsuperscript{12} Moreover, TMDCs play an essential role in flexible nanoelectronics for their higher charge mobility and strain limits than conventional flexible electronics.\textsuperscript{13} However, large single-crystal CVD growth of monolayer TMDCs film with high mobility for transistor applications still remains a challenge.\textsuperscript{14–20}

Recently, “liquid state” molten glass has been utilized as a growth substrate for TMDCs film growth, and a large-size monolayer MoSe$_2$ single-crystal on molten glass has been demonstrated for the first time.\textsuperscript{21} Batch production of 6-in. uniform monolayer MoS$_2$ on molten glass was developed, with a single-crystal edge length larger than 400 $\mu$m, with the mobility and on/off ratio ranging from 6.3 to 11.4 cm$^2$/V·s and 10$^4$ to 10$^5$, respectively.\textsuperscript{22} Both of these results reveal that the defect-free and smooth surface of molten glass provides a good platform for TMDCs film growth.\textsuperscript{23} Despite these progress, further studies and optimizations of the MoS$_2$ single-crystal grown on molten glass and its electrical properties are still needed.

In this work, we report an approach for growing large single-crystal MoS$_2$ monolayer using an optimized atmospheric pressure chemical vapor deposition (APCVD) method. Moreover, molten glass is utilized as a growth substrate for providing a “liquid-state” surface, which can significantly reduce defect sites, suppress nucleation density, and facilitate large domain growth, compared with conventional c-plane sapphire. The MoS$_2$ monolayer exhibits a size modulation by growth temperature with the maximum single-crystal size up to 563 $\mu$m on molten glass at a growth temperature of 850 °C in 10 min. Monolayer MoS$_2$ film is transferred onto a high-{$\kappa$} dielectric substrate via PMMA-assisted method for high-performance transistor fabrication. These MoS$_2$ exhibit 10$^9$ to 10$^{10}$ on/off ratio, which is more than two orders of magnitude higher than that transferred from c-plane sapphire. The intrinsic field-effect mobility reaches up to 84 cm$^2$/V·s at 20 K and 24 cm$^2$/V·s at 300 K, which is twofold compared with that transfer from c-plane sapphire as well. This low-cost, high-quality, and large domain growth technique of 2D TMDCs provides a pathway for high performance 2D electronic devices.

Monolayer MoS$_2$ domains were grown on molten glass or c-plane sapphire substrates by a modified APCVD process. First, a piece of 1 × 1 cm$^2$ molten glass or sapphire was cleaned with acetone, isopropanol alcohol (IPA), and deionized water, followed by 5 min O$_2$ plasma cleaning under medium power (10 W). Then, 1.3 mg MoO$_3$ powder was added next to the substrate with a distance of 2 mm, which was able to provide a relatively high concentration of MoO$_3$ precursor. Fewer MoO$_3$ weight will cause MoO$_3$ vapor insufficient. A ceramic chip was capped on the top of MoO$_3$ powder to reduce the exposure area for preventing “source poisoning.” They were put into a 3-in. three-zone furnace together with a ceramic boat carrying 1.4 g sulfur powder as depicted in Fig. 1(a). The distance from the substrate to the sulfur powder kept at 50 cm. The base vacuum was pumped down via a mechanical pump below 30 mTorr. Then, the angle valve was shut and 1000 sccm Ar was introduced to increase pressure until 1 atm. The three-zone furnace temperature was risen up to 230/350/800 °C as depicted in Fig. 1(b) with a growth time of 10 min. The angle valve was adjusted manually for maintaining the pressure at 1 atm during the whole process.

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As depicted in Figs. 1(c) and 1(d), MoS$_2$ single-crystals grown on molten glass at 800 °C show clean and uniform triangle shape, while smaller MoS$_2$ single-crystals with an irregular edge and uneven size are obtained from the c-plane sapphire substrate. The majority of MoS$_2$ domain sizes on molten glass is 52 μm, 2.4 times larger than on the sapphire substrate, as depicted in Fig. 1(e). We attribute the improvements to the lower defect sites and more smooth “liquid state” surface of melted glass than sapphire, which can significantly reduce nucleation density and facilitate large domain growth. Moreover, the smooth surface of melted glass assists the precursor in diffusing faster and by-product discharging faster beneath the boundary layer.21 Besides, the Na element in soda-lime glass (i.e. molten glass) is a growth boost as well for lowering the energy barrier in vapor reaction.22 The step height measured by AFM is found to be 0.86 nm, consistent with the monolayer property, as depicted in Fig. 1(f).

The growth temperature is related to the reaction kinetic energy, which affects the growth rate and size directly. As shown in Fig. 2(a), the domain size first increases and then decreases with growth temperature. A similar trend was not found on sapphire substrate. As depicted in Fig. 2(b), the largest single-crystal size up to 563 μm was obtained at 850 °C, where MoO$_3$ precursor supply is fast and thereby results in concave edges, indicating an S-insufficient situation.24 A similar situation happens in 825 °C for a high growth rate, indicating more sulfur vapor supply is needed for a regular and defect-free MoS$_2$ single crystal. It is well known that the higher temperature results in a higher sublimation rate of MoO$_3$ as well as faster growth on the substrate.25 As the temperature increases from 800 to 850 °C, the reaction rate on substrate increases and dominates the single-crystal growth, corresponding to a larger single-crystal size. As the temperature increased further to 900 °C, the sublimation rate of MoO$_3$ dominates with lower vapor pressure, contributing a smaller single-crystal size. Raman and photoluminescence (PL) spectra were used to characterize the monolayer MoS$_2$ as-grown on molten glass and transferred on 300 nm SiO$_2$/Si. As shown in Fig. 2(c), $E_{2g}^1$ and $A_{1g}$ peaks located at 384.2 and 401.8 cm$^{-1}$, respectively. The frequency difference between these two peaks is 17.6 cm$^{-1}$, corresponding to monolayer MoS$_2$. After transferred onto SiO$_2$/Si substrate, the $E_{2g}^1$ peak remained almost unchanged (384.3 cm$^{-1}$), while the $A_{1g}$ peak blue shifted (403.2 cm$^{-1}$) and the peak full-width half-maximum (FWHM) shrank. Figure 2(d) shows the PL spectrum comparison of monolayer MoS$_2$ single-crystal before and after transfer as well. Before transfer, the $A$ exciton peak located at 1.84 eV, consistent with the reported value for monolayer MoS$_2$.26 After transfer, the $A$ exciton peak intensity shows a 5 times higher promotion and a peak blueshift of 10 meV. The $A_{1g}$ peak blueshifts, FWHM shrinks, $A$ exciton blueshifts, and intensity enhancement all originate from the tension stress release after transfer.27 The tension stress is generated from the molten glass melted and solidified during growth and cooling stages.

In order to demonstrate the superiority of molten glass compared to c-plane sapphire, MoS$_2$ FETs were fabricated from these two growth substrates. High-$\kappa$ dielectrics were applied for reducing equivalent oxide thickness (EOT) and achieving tighter electrostatic control by global back gate.28 18 nm HfLaO was deposited on cleaned highly degenerated $P$-type Si by atomic layer deposition (ALD) with a relative dielectric constant of around 26.6. As-grown MoS$_2$ single-crystals on molten glass were transferred onto 18 nm
HfLaO/Si substrate via the PMMA-assisted method with 30 wt. % KOH solution as the etchant. MoS₂ transistors were fabricated as shown in the schematic view in Fig. 3(a). Electron beam lithography (EBL) and reactive ion etch (RIE) were utilized for isolation as $50 \times 10 \times 10^{-6} \mu m^2$ rectangle stripes. E-beam evaporation (EBE) was then applied for S/D ohmic contact with nickel/gold (20/60 nm) deposition. Channel lengths ranged from 0.5 to 3 µm for extracting contact resistance.

For a fair comparison between MoS₂ based on molten glass and c-plane sapphire, 500-nm channel length transistors’ transfer and output characteristics curves were measured, as shown in Figs. 3(b) and 3(c). The CVD MoS₂ transistor transferred from molten glass exhibits a two orders of magnitude higher on/off ratio ($10^8$) and a higher ON current, indicating the electrical advantage of the MoS₂ based on molten glass. The maximum drain current is around 135 µA/µm as shown in the output characteristics in Fig. 3(c) at $V_{bg} = 3$ V and $V_{ds} = 2$ V. The ON current increases from 17 to 123 µA/µm⁻¹ as the channel length decreases from 3 to 0.5 µm, with a high on/off ratio of more than $8 \times 10^8$ as depicted in Fig. 3(d).

In order to further investigate the transport properties, the low-temperature measurement was carried out from 300 K to 4.3 K as depicted in Fig. 4(a), where $I_{on}$ monotonically increased and with a positive threshold voltage shift as temperature decreases. The current improvement can be attributed to the increasing mobility due to the reduced phonon scatterings at low temperature while the positive threshold voltage shift can be attributed to the frozen trap charges at the oxide/MoS₂ interface at low temperatures. The current improvement can also be observed from the output characteristics at higher drain biases as depicted in Fig. 4(b), where more than 39% current improvement can be observed with $V_{bg} = 3$ V and $V_{ds} = 2$ V at 4.3 K.

Figure 4(c) shows a systematic study of $I_{on}$ with different channel lengths at varying temperatures. The current increases as the channel length scales down as in conventional transistors. To further investigate the carrier transport property, intrinsic field-effect mobility at different temperatures through removing contact resistance was extracted as depicted in Fig. 4(d). The mobility at room temperature is $24 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ($C_{ox}$ = 0.85 µF/cm²), which is more than 12 times higher than that transferred from c-plane sapphire. This improvement indicates that molten glass as the growth substrate provides much higher quality MoS₂ films than c-plane sapphire. When temperature decreases from 300 to 100 K, the mobility increases from 24 to 64 cm²V⁻¹s⁻¹. The mobility relation with temperature fitted by $\mu \sim T^\gamma$ results in a $\gamma$ of 1.28, which is less than the theoretical value ~1.69 in the monolayer, indicating that the HfLaO substrate can effectively lower interface phonon scattering. When the temperature further decreases from 100 to 4.3 K, the mobility increases at a much slower rate with the maximum mobility of 84 cm² V⁻¹ s⁻¹ at 20 K, where phonon scattering becomes negligible while Coulomb scattering dominates in that temperature region.

In conclusion, this letter reports the synthesis of large area single-crystal monolayer MoS₂ based on molten glass growth and its electrical characteristics. A modified APCVD method is utilized in this study with molten glass as the growth substrate for its “liquid state” surface. MoS₂ grown on molten glass exhibits a larger size and more regular edge than on c-plane sapphire, with the largest single-crystal size up to 563 µm at 850°C. Devices fabricated using single-crystal monolayer MoS₂ on the 18 nm HfLaO substrate exhibit better performance than those based on c-plane sapphire. Intrinsic field-effect mobility up to $24 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature and $84 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 20 K has been achieved. These results show that optimized growth substrate and dielectrics have the potential to provide improved electrical performance for future electronic devices based on TMDCs.
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