Rapid fabrication of submillimeter ultrathin CdI$_2$ flakes via a facile hot plate-assisted vapor deposition method

Mei Zhao, Liang Qiao*
School of Physics, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, P. R. China
E-mail: liang.qiao@uestc.edu.cn

Abstract. As an important member of cadmium-based halides, two-dimensional (2D) CdI$_2$ has drawn widespread attention due to its excellent optoelectronic properties. However, the large-size growth of ultrathin CdI$_2$ flakes remains a huge challenge. Here, a facile hot plate-assisted vapor deposition (HPVVD) method is developed to synthesize submillimeter ultrathin CdI$_2$ flakes. The photodetectors based on CdI$_2$ flakes exhibit extremely low dark current (0.53 pA), ultrafast response speed (<2 ms) and good stability. The proposed HPVVD method may open a new avenue to prepare 2D layered metal halides.

1. Introduction

2D layered metal halides have attracted increasing attention recently in the fields of optics, electronics and magnetism, owning to high absorption coefficient, direct bandgap and spin freedom properties [1]. Cadmium-based halides (CdX$_2$: X = I, Br, Cl), as typical metal halides, have been studied widely in light emitting devices and ultraviolet optoelectronic devices because of layered van der Waals (vdW) structure, wide band gap and excellent luminescent properties [2,3]. Specially, CdI$_2$, has gained dramatical research interest in luminescence, mainly thanks to its remarkable properties including intrinsic n-type semiconductor, wide band gaps, and strong optical absorption [4].

Currently, three main methods have been used for preparing 2D CdI$_2$, namely chemical bath deposition, thermal evaporation, and horizontal physical vapor deposition (PVD) [3,5,6]. However, the chemical bath deposition method is generally complex and time-consuming, resulting in irregular morphology, poor crystallinity and small size of the products; the thermal evaporation method suffers from thick, uneven and amorphous samples; although horizontal PVD has been recently adopted to grow high-quality 2D CdI$_2$ nanosheets, the small size, thick thickness, and harsh preparation conditions are inevitably caused. Therefore, it is urgent to develop a simple and efficient preparation approach to synthesize large-area, large-size, ultrathin 2D CdI$_2$ high-quality single crystals, in order to meet the practical application in semiconductor industry in future.

Herein, a facile HPVVD approach has been developed to synthesize large-area, submillimeter-size, ultrathin CdI$_2$ flakes with high quality on mica substrates. The resulting CdI$_2$ flakes with preferred (001) crystal plane are high-quality single crystals, which have been proved by a series of characterizations. Moreover, the photodetectors based on individual CdI$_2$ flake show excellent ultraviolet photoelectric properties, such as extremely low dark current (0.53 pA), high on/off current ratio (56.70), high responsibility (5.55 mA/W), ultrafast response speed (<2 ms) and good stability.
2. Experimental section

2.1 Synthesis of CdI2 flakes: First, trace amounts of CdI2 powder was placed on clean glass sheets and put together on a hot plate. Meanwhile, another two glass sheets with thickness of 1 mm were placed on either side of the above glass sheet as a bracket for mica substrate. The temperature of the hot plate is then raised to the set temperature (360-400°C), and CdI2 flakes began to grow on the mica immediately. The whole growth process taken only 1-2 min in air at room temperature. Except for mica, CdI2 flakes can also grow on SiO2/Si and quartz substrates.

2.2 Characterization of CdI2 flakes: The morphology, size and thickness of CdI2 flakes were characterized by optical microscope (OM) and atomic force microscope (AFM). The crystal structure, phase and chemical composition, fluorescence and optical absorption of the samples were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system, Raman and UV-vis absorption spectrum.

2.3 Fabrication and performance measurement of CdI2 devices: The CdI2 flakes-based photodetectors were fabricated by transfer electrodes method. In short, Au electrodes, which were firstly deposited on a SiO2/Si substrate by the thermal evaporation machine (Nexdep, Angstrom Engineering), were peeled off assisted by the liquid metal Ga and transferred to the desired CdI2 flake. The photodetection test was performed on the probe station (Lakeshore, TTPX) connected to a semiconductor device analyzer (Keysight, B1500A) and 365 nm laser.

3. Results and Discussion

Figure 1a shows the HPVVD experimental setup, which is quite simple devoid of harsh experimental conditions as required by traditional PVD. As shown in Figure 1(b, c), CdI2 is a typical layered material with a hexagonal unit cell, and belongs to space group P63mc (186) with lattice constants of a = b = 4.25 Å, c = 13.73 Å. Large-area CdI2 flakes are grown on the mica substrate, displaying regular triangular or hexagonal geometry (Figure 2d). Note that the maximum lateral size of CdI2 flakes can reach tens or even hundreds of microns (Figure 2e-f), which is larger than conventional PVD-based CdI2 flakes [6]. In addition, the thickness of ultrathin CdI2 flakes can be thin down to about 0.68 nm (Figure 2g), which corresponds to the thickness of monolayer CdI2.
Figure 1. Growth and characterizations of CdI$_2$ flakes. (a) Schematic of HPVVD setup for growth of CdI$_2$ flakes on mica. (b, c) The crystal structure of CdI$_2$ from side and top view, respectively. (d) The OM image of large-area CdI$_2$ flakes. (e, f) The typical OM images of large-size CdI$_2$ flakes with triangular and hexagonal shape, respectively. (g) AFM image of monolayer CdI$_2$.

Figure 2. Crystal structure and optical properties of CdI$_2$ flakes. (a) XRD pattern. (b) HRTEM image. Inset is the corresponding SAED pattern. (c) EDS spectrum. (e) PL spectrum. (d) Raman spectrum. Inset: the OM image and Raman intensity mapping ($E_g$ and $A_{1g}$ mode) of a triangular CdI$_2$ flake. (f) UV-vis absorption spectra.
Figure 2a displays the XRD patterns of CdI$_2$ flakes. Four sharp XRD peaks can all be well indexed to \{001\} family planes ((002), (004), (006), (008)) of hexagonal phase CdI$_2$ (PDF#33-0239), suggesting the (001) plane preferred orientation and high crystalline quality of CdI$_2$ flakes. As exhibited in Figure 2b, the HRTEM image and the corresponding SAED pattern show clear lattice fringes and only single set of sharp diffraction spots in hexagonal symmetry, further indicating the excellent single crystalline nature of CdI$_2$ flakes. The lattice spacing with 0.37 nm is corresponded to (110) family planes, suggesting (001) plane is the preferred growth orientation, in accordance with the XRD results. The corresponding EDS spectrum (Figure 2c) demonstrates strong signals of Cd and I with atomic ratio close to stoichiometric ratio of CdI$_2$ (1:2). The Raman spectrum of CdI$_2$ flakes (Figure 2d) presents two prominent peaks around 45 and 110 cm$^{-1}$, corresponding to the in-plane (E$_g$) and the out-of-plane (A$_{1g}$) phonon vibration mode, respectively, in conformity to the recently reported 2D CdI$_2$ crystals [4,6]. The inset is the typical Raman intensity maps of E$_g$ and A$_{1g}$ modes, confirming highly uniform crystalline quality of CdI$_2$ flake. In addition, the PL spectrum in Figure 2e reveals a distinct peak centered at 415 nm, corresponding to a bandgap of 2.99 eV. Furthermore, the optical bandgap can be calculated by the Tauc equation: 
\[
\alpha h\nu = A(h\nu-E_g)^m,
\]
where $\alpha$, $h$, $\nu$, and $m$ is the effective absorption coefficient, the Planck constant, the frequency of the light, and absorption index. The optical bandgap of the CdI$_2$ flakes is estimated to be 2.98 eV by extrapolating the linear portion on the plots, as shown in Figure 2f. The above results confirm the high-quality crystalline feature of the CdI$_2$ flakes.

As shown in Figure 3a, the CdI$_2$ flake-based photodetector was constructed. Figure 3 (b, c) demonstrates I-V and I-T curves under the dark and 365 nm laser illumination with different power intensity, indicating remarkable photoresponse. Specially, the device reveals an ultralow dark current (0.53 pA) even at $V_{bias} = 5$ V. The corresponding on/off current ratio is 56.70 under 16.66 mW/cm$^2$. On basis of the equation: 
\[
R = \frac{I_{ph}}{PS},
\]
where $I_{ph}$, $P$, $S$ represent photocurrent, light intensity, and effective illuminated areas, respectively, the responsivity ($R$) can be reach up to 5.55 mA/W. Moreover, the photocurrent as a function of the power density is fitted as $I_{ph} = aP^{0.97}$ (Figure 3d), implying the photocurrent is dominated by photoconductive mechanism. In addition, the repeatable photocurrent is displayed in Figure 3e, suggesting the good stability of the device. Furthermore, the obtained rising and decay time from enlarged I-T curve is $< 2$ ms, is shown in Figure 3f. Thus, the outstanding optoelectronic performance is ascribed to the high-quality single-crystalline feature of CdI$_2$ flakes.
Figure 3. Optoelectronic performance of CdI$_2$ flake-based photodetector. (a) Schematic of the photodetector based on CdI$_2$ flake; (b) $I$-$V$ curves measured under dark and 365 nm laser illumination; (c) The power density-dependent photoresponse at $V_{bias} = 5$ V; (d) The corresponding fitting curve of photocurrent versus power density; (e, f) The photoresponse to on/off laser irradiation show (e) the stability (f) the response rate.

4. Conclusion
In summary, large-size ultrathin CdI$_2$ flakes with high quality were successfully synthesized by a facile HPVVD method for the first time. The CdI$_2$ flakes-based photodetectors achieve outstanding optoelectronic performance, including extremely low dark current (0.53 pA), high on/off current ratio (56.70), high responsibility (5.55 mA/W), ultrafast response speed (<2 ms) and good stability, implying potential application in optoelectronics. This work provides a simple approach to grow 2D metal halides.

Acknowledgements
This work was supported by the National Natural Science Foundation of China (Grant No. 1174044) and the Young 1000-talent Program.

References
[1] Wang F, Zhang Z, Zhang Y, et al. (2020) Honeycomb RhI$_3$ Flakes with High Environmental Stability for Optoelectronics. Adv. Mater., 32(25): 2001979.
[2] Fujita M, Nakagawa H, Matsumoto H, et al. (1990) Optical Spectra of Cadmium Halide Crystals in 3-30 eV Region. J. Phys. Soc. Jpn., 59(1): 338-347.
[3] Yahia I S, Shapaan M, Ismail Y AM, et al. (2015) Thickness dependence of structural and optical properties of cadmium iodide thin films. J. Alloys Compd., 636: 317-322.
[4] Yan Z, Yin K, Yu Z, et al. Pressure-induced band-gap closure and metallization in two-dimensional transition metal halide CdI$_2$. (2020) Appl. Appl. Mater. Today, 18: 100532.
[5] Kariper I A. Structural, optical and porosity properties of CdI$_2$ thin film. (2016) J. Mater. Res. Technol., 5(1): 77-83.
[6] Ai R, Guan X, Li J, et al. Growth of Single-Crystalline Cadmium Iodide Nanoplates, CdI$_2$/MoS$_2$ (WS$_2$, WSe$_2$) van der Waals Heterostructures, and Patterned Arrays. (2017) ACS Nano, 11(3): 3413-3419.