Rare Metal Materials and Engineering
Volume 51, Issue 8, August 2022
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Wang Xiyang, Hao Qunqing, Zhang Yun, et al. Preparation and Characterization of High-Quality USb_2 Thin Films on Graphene/6H-SiC(0001)[J]. Rare Metal Materials and Engineering, 2022, 51(08): 2721-2726.

LETTER

Preparation and Characterization of High-Quality USb_2 Thin Films on Graphene/6H-SiC(0001)

Wang Xiyang, Hao Qunqing, Zhang Yun, Pan Qifa, Chen Qiuyun, Feng Wei, Wang Yonghuan, Zhu Xiegang, Luo Lizhu, Lai Xinchun, Liu Qin, Tan Shiyong

Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang 621908, China

Abstract: Heavy fermion systems can exhibit abundant attractive quantum ground states by tuning external parameters such as dimension. High-quality USb_2 thin films were prepared on graphene/6H-SiC(0001) surface by molecule beam epitaxy. Combining the reflection high energy electron diffraction, X-ray diffraction, electric transport and X-ray photoelectron spectroscopy measurements, it is demonstrated that the grown USb_2 films are high-quality single crystals. Furthermore, the surface topography, atomic structure and band structures of USb_2 films were characterized by scanning tunneling microscopy (STM) and angle-resolved photoelectron spectroscopy (ARPES). Results show that the surface atomic structure, electric transport property and band structure of the grown USb_2 films are similar to those of bulk USb_2 single crystals. The preparation and characterization of high-quality USb_2 films provide precious experimental experiences for exploring fantastic properties of low-dimensional uranium-based heavy fermion systems by growing ultrathin films with desirable thickness in the future.

Key words: USb_2 thin films; STM; ARPES; electronic structure

As typical examples of strongly correlated electron systems, heavy fermion materials exhibit diverse quantum ground states such as magnetic order[1-3], unconventional superconductivity[4], hidden order[5] and topological phase[6] due to the competition between Kondo spin screening and RKKY long-range magnetic exchange. Because of the properties of f electrons[7], heavy fermion systems have relatively small characteristic energy scales, which allow the acquirement of various quantum states by tuning external parameters such as pressure[8], magnetic field[9], chemical doping[10] and dimension. Antiferromagnetic USb_2 provides an ideal platform for such studies, with a high antiferromagnetic transition temperature exceeding 200 K[11,12]. By applying pressure[8] and magnetism[9], USb_2 exhibits quantum critical behavior. And the kink structure of the electron band near the Fermi level is also observed[13,14]. Our previous results observed two different kinds of nearly flat bands in the antiferromagnetic state of USb_2. One is driven by the Kondo interaction between 5f electrons and conduction electrons, and the other originates from the magnetic order[3].

In general, many-body correlation effects become more important and complex at lower spatial dimensions. Moreover, both thermal and quantum fluctuations are greatly enhanced with the reduction of dimension. Therefore, if the dimensions of heavy fermion materials can be controllably adjusted to prepare low-dimension system, like quasi two-dimensional ultrathin films[15-17], it is expected to acquire more attractive exotic quantum properties. Previous studies on heavy fermion thin films have mainly focused on rare-earth based materials, such as pure La[18] and Ce[19-21] films and Ce/Yb-based systems[22,23]. So far, there are few reported studies on successful preparation of uranium-based thin films, including pure uranium[24,25] and UPd_2Al_3[26,27] thin films. In general, successful examples of preparing high-quality thin films of U-based compounds are extremely scarce at present. Consequently, mastering the method of growing high-quality U-based films undoubtedly provide a precious chance to study the dimensional effects on heavy fermion systems and to

Received date: January 18, 2022
Foundation item: National Key Research and Development Program of China (2017YFA0303104); National Natural Science Foundation of China (11904335, 11974319, 21903074, 11774320, 11904334, 12122409, 11874330); Special Funds of Institute of Materials (TP02201905)
Corresponding author: Liu Qin, Ph. D., Professor, Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang 621908, P. R. China, E-mail: liuqin493@163.com

deepen the understanding of various physical problems and novel quantum effects in them.

Benefiting from the emergence and development of molecular beam epitaxy (MBE) technology, it has become feasible to grow high quality thin films of lanthanide heavy fermion compounds[28] and many novel quantum effects have been found in those thin films. Nevertheless, as an important representative of actinide elements, uranium has high evaporation temperature and is toxic, radioactive, and highly active, which pose many challenges to grow U-based high-quality thin films. Specifically, conventional evaporation sources and crucible cannot be used for the growth of U-based materials, because of the high activity of U with which many conventional materials can react. Furthermore, MBE growth of high-quality films of multielement compounds requires the simultaneous participation of two or more elements. Therefore, it is more difficult to grow high-quality thin films of compounds compared to single element. In the present work, we prepared USb_2 single-crystal thin films by MBE method after exploring a series of growing profiles and persistently optimizing the evaporation parameters. Then reflection high energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurement were carried out to monitor the quality of the growing thin films. Electrical transport, scanning tunneling microscopy (STM), and angle-resolved photoelectron spectroscopy (ARPES) studies were performed and the measured properties were compared with those of bulk single crystal, showing that the grown USb_2 is a relatively high-quality film. The ability of proficiently growing high-quality single-crystal films of U-based binary compounds will be greatly beneficial for investigating the effects of dimensional control on the properties of U-based heavy fermions systems in the future.

1 Experiment

USb_2 high-quality thin films were grown by vapor deposition of uranium and antimony on graphene/6H-SiC (0001) surface by MBE method. To be specific, the flux ratio of U and Sb obtained by quartz crystal oscillator was controlled at about 1∶25. During the growth, the temperature of graphene substrate was kept at about 580 °C, and the base pressure of MBE chamber was kept below 6×10^{-7} Pa. Since the saturated vapor pressure of Sb is much higher than that of U, the adopted evaporation temperature of U was much higher than the substrate temperature, whereas the latter was set slightly higher than the sublimation temperature of Sb based upon the three-temperature rule[29-31], i.e. $T_U>>T_{sub}>T_{Sb}$. Under such condition, the excess Sb will be desorbed from the substrate except for those reacted with U to form compounds. Besides, as long as the ionic flux of Sb is much larger than that of U, USb_2 phase will be the only product according to the phase diagram of U-Sb[32].

During the growth of USb_2 film, we combined RHEED to in-situ monitor its quality under ultrahigh vacuum environment. Then we used ex-situ XPS measurement to determine the composition ratio of the film. In order to determine the crystal structure of the film, ex-situ XRD measurement was conducted at 300 K with Cu Kα (λ = 0.154 056 nm) radiation under ambient pressure. The electrical resistivity was detected by the standard four-probe method in a commercial physical property measurement system (PPMS). The contacts were made by pressing indium method quickly. In addition, to obtain topographic images, we used a constant tunneling-current mode at a fixed sample bias voltage by STM, and the base pressure of the STM analysis chamber was better than 1×10^{-9} Pa, while the pressure before annealing in the pretreatment chamber was about 4×10^{-9} Pa, which was better than 1×10^{-8} Pa during annealing. The as-grown film was annealed until clear RHEED stripes appeared, and then it was transferred into ARPES analysis chamber with a base pressure lower than 7×10^{-9} Pa. ARPES measurements were conducted with 21.2 eV photons from a helium discharge lamp. The energy resolution and angular resolution are 10 meV and 0.2°, respectively. A freshly evaporated gold sample in electrical contact with the La films was served to calibrate E_F.

2 Results and Discussion

USb_2 crystallizes in the tetragonal structure of anti-Cu_2Sb type, which orders antiferromagnetically below a high Néel temperature of 203 K. As the lattice structure of USb_2 does not match well with that of SiC, we annealed the SiC substrate by a standard method to obtain the graphene surface to grow USb_2 films. As expected, the weak van der Waals bonding between graphene and USb_2 layers effectively reduces the lattice mismatch effect. The crystal structure of USb_2 and schematic diagram of the epitaxial growth process are shown in Fig.1a. The RHEED patterns of graphene/6H-SiC(000l) and USb_2(00l) surface are shown in Fig.1b and 1c, respectively. It can be seen that the stripes of USb_2(00l) film are relatively clear and sharp, indicating a good film quality, just like the reported case of SnTe films grown on graphene/6H-SiC[33]. Fig. 1d shows the XRD pattern of the USb_2 thin films measured at room temperature and ambient pressure. The characteristic peaks are similar to that of bulk single crystal[3], which proves that the grown film is a high-quality single crystal and (00l) orientated without other phases. Fig. 2e shows measured electrical resistivity ρ versus T for USb_2 film. The overall trend of the ρ-T curve is highly similar to that of bulk single crystal[3]. The characteristic antiferromagnetic phase transition temperature of the grown film is 199 K, which is very close to the Néel temperature of 203 K observed in bulk single crystal.

Fig. 2a and 2b show the XPS spectra of ex-situ Sb 3d/O 1s and U 4f of the grown film before and after Ar^+ sputtering, respectively. The original Sb 3d/O 1s spectrum, as shown by the red line in Fig. 2a, exhibits double-peak structure at 528.2 and 530.4 eV, which indicates the existence of metallic Sb and Sb_2O_3, respectively. The peak at the 530.4 eV is abnormally high resulting from the overlap of the Sb $3d_{5/2}$ peak of Sb_2O_3 and O 1s peak. The original U 4f spectrum shows that almost all the uranium is oxidized. Obviously, U is much more highly

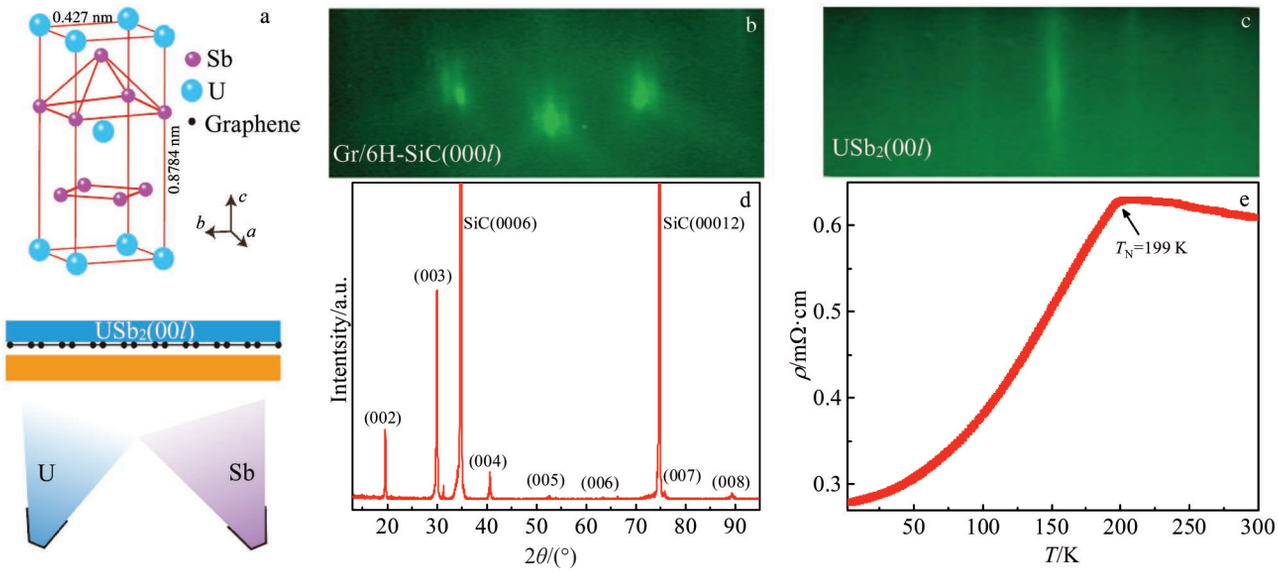

Fig.1 Film quality, surface structure and electrical resistivity of USb_2: (a) crystal structure of USb_2 (upper panel) and schematic structure of the USb_2 (00*l*) film on the graphene (Gr)/6H-SiC(000*l*) surface grown by the MBE method (lower panel); RHEED patterns of Gr/6H-SiC (0001) surface (b) and the grown USb_2 films (c); (d) XRD pattern of the as-grown USb_2 films at room temperature and atmospheric pressure; (e) temperature dependence of electrical resistivity ρ along the *a* axis of USb_2 film (T_N represents Néel temperature)

oxidized than Sb, revealing an interesting oxidation mechanism of the sample. The oxidation is reasonable because before transferring into XPS chamber, the sample was exposed to air for a short period of time. After 30 s of Ar^+ sputtering, the intensities of the oxide peaks decrease significantly, indicating that most oxides are removed and the thickness of the oxide layer is on the order of 10^1 nm. Ultimately, after 60 s Ar^+ sputtering, all the oxides are removed which is supported by the disappearance of O 1s peak. The Sb $3d_{5/2}$ is at 527.5 eV, lower than that of the metallic Sb $3d_{5/2}$ (528.2 eV), indicating that Sb possesses negative valence state. Dividing the peak area with appropriate sensitive factor, the atomic ratio of U and Sb is determined to be approximately 1∶2, proving that the grown film is USb_2 indeed[34].

The effect of annealing on the quality of USb_2 film was studied by STM. Fig. 3a shows the typical topographic STM image of the unannealed film. Small islands coexist with a large number of disordered structures. Fig. 3b shows the topography of the film after annealing at 700 °C for 2 h. The number of ordered islands distinctly increases, but a few disordered structures still exist. Fig. 3c shows the topography after annealing for 4 h, and it can be seen that there are only clean and well-ordered flat islands, implying that annealing at high temperature for a long time can effectively improve the film quality at the nanoscale. Fig.3d is the atomically resolved topographic image, which clearly shows that the film has a tetragonal lattice. The measured height profile in Fig. 3e reveals that the lattice parameter of USb_2(001) surface is 0.43 nm, which is consistent with the value in USb_2 single crystal (*a* =*b*=0.4270 nm) within the allowed error range. As shown in Fig.3f, the step height of two neighboring layers of the film is

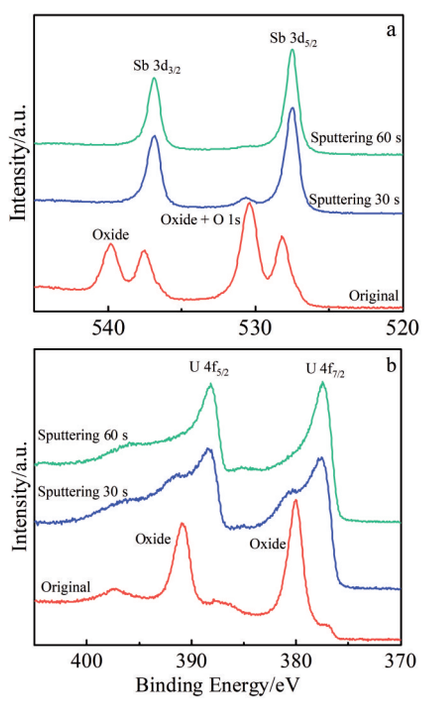

Fig.2 XPS spectra of USb_2 film before and after sputtering for 30 and 60 s: (a) Sb 3d and (b) U 4f

0.87±0.03 nm, which agrees well with the lattice constant of 0.8784 nm along *c*-axis of USb_2 single crystal.

Fig.4 shows the band structures of USb_2 thin film as well as the bulk single crystal measured at 80 K by ARPES. The photoemission intensities measured around Γ point and along Γ-M directions over a large energy scale are presented in Fig. 4a and 4b, respectively. The band structures are very similar to

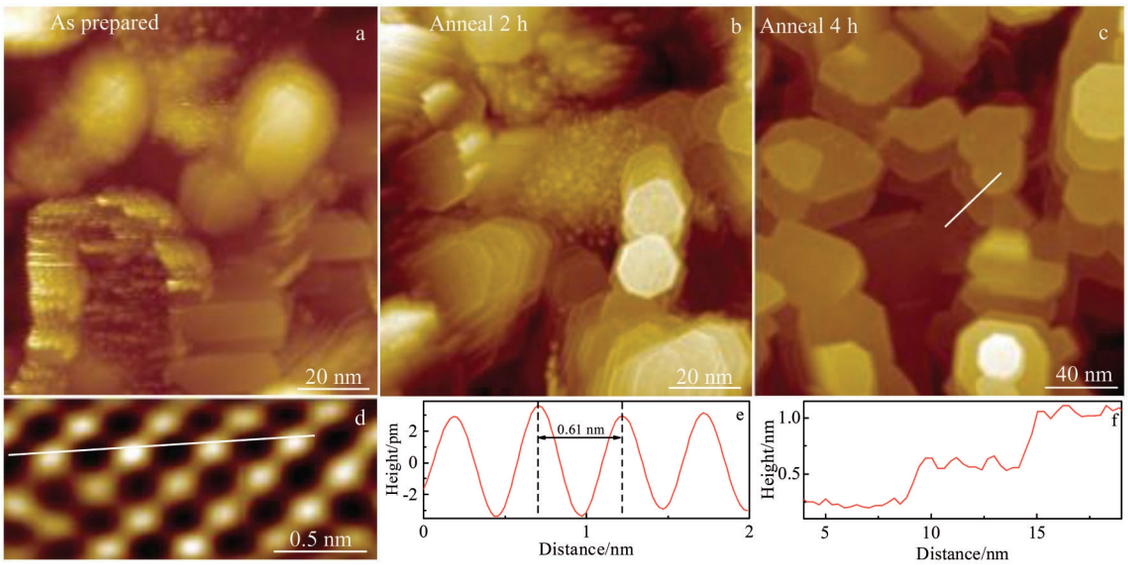

Fig.3 Large-scale topographic STM images of the grown USb_2 film before (a) and after annealing at 700 °C for 2 h (b) and 4 h (c) (V_b=1 V, I_t= 100 pA); (d) atomically resolved topographic image after inverse-filtering of the USb_2 (001) surface (V_b=5 mV, I_t=2.5 nA); (e) height profile showing the interatomic spacing on USb_2(001) film measured along the white line in Fig.3d; (f) height profile showing the step heights between neighboring USb_2 layers taken along the white line in Fig.3c (all the STM measurements were conducted at 77 K)

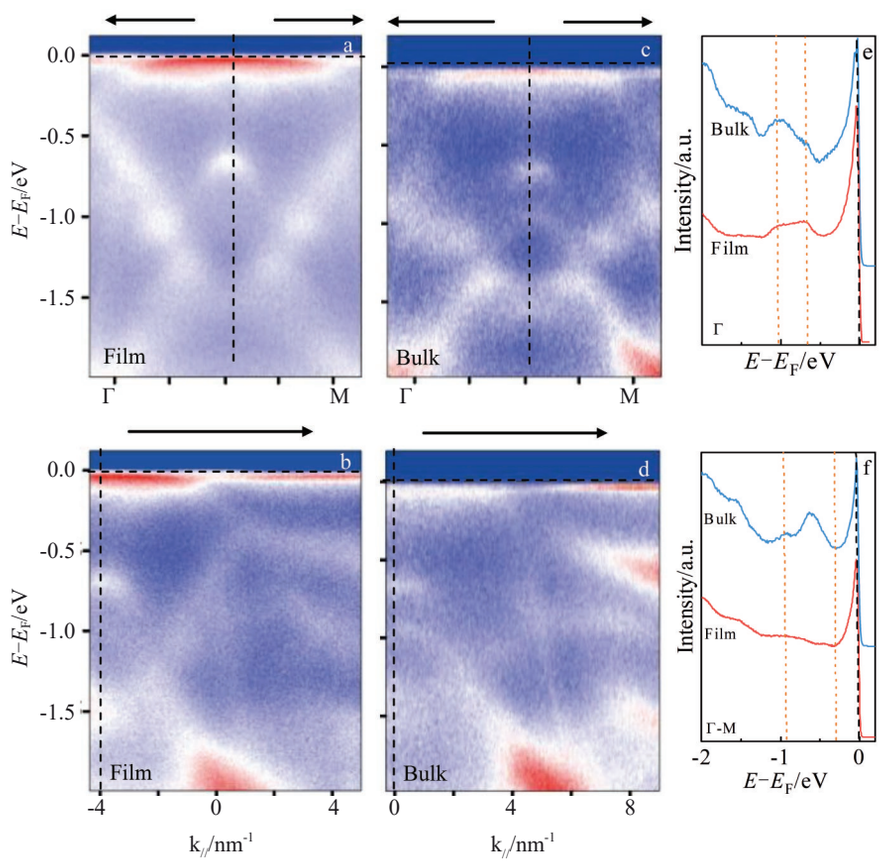

Fig.4 Comparison of the band structures of the USb_2 film (a, b) and bulk single crystal (c, d) around high symmetric Γ point (a, c) and along Γ-M direction (b, d); comparison of the EDCs of USb_2 film and bulk single crystal at Γ point (e) and along Γ-M direction (f) (red dashed lines track the energy positions of the peaks and dips in the EDCs of USb_2 films and bulk single crystals; all the data were measured at 80 K using 21.218 eV photons)

the results of bulk USb_2 single crystal shown in Fig.4c and 4d, indicating that the quality of USb_2 film is relatively high. Lots of highly dispersive bands originated from itinerant conduction electrons (U 6d and Sb 5p electrons) exist at high binding energies below −0.3 eV. Two nearly flat bands are observed around the Γ and M points, which are mainly contributed from the U 5f electrons. Fig. 4e shows the integrated energy distribution curves (EDCs) of USb_2 in Fig. 4a and 4c, while Fig. 4f shows the integrated EDCs of USb_2 in Fig.4b and 4d. Comparing the EDCs of thin film and bulk USb_2 single crystal, we can see that these peaks and dips locate at the same energy levels as marked by the red dashed lines, but their relative intensity distributions are slightly different. Two extremely sharp photoemission peaks can be observed in the vicinity of E_F, which are mainly originated from the hybridization between the 5f electrons and conduction electrons. It is an interesting topic to know how the characteristic hybridization transition temperature changes with decreasing film thickness in USb_2, which deserves systematic study in the near future.

3 Conclusions

1) The successful growth of high-quality USb_2 thin films on graphene/6H-SiC(0001) surface is achieved by molecular beam epitaxy method.

2) Ex-situ XPS measurements find that Ar^+ sputtering can effectively remove the oxides on outer surface, and the atomic ratio of U∶Sb is determined to be approximately 1∶2, proving that the grown film is USb_2 indeed.

3) XRD data demonstrates that the film is (00*l*) orientated without other phases. The electrical resistivity as a function of temperature of USb_2 film is very similar to that of bulk single crystal.

4) In-situ STM measurements suggest that the surface flatness and the ratio of well-ordered island structures of USb_2 films can be greatly improved by annealing at appropriate high temperatures for enough time. The surface topography and structure analysis show that the step height of the film is consistent with the lattice constant of USb_2 along *c*-axis and the in-plane surface lattice parameter accords with that on bulk USb_2(001) plane.

5) ARPES results show that the band structures around Γ point and along Γ-M directions of USb_2 thin films are very similar to the results of bulk USb_2 single crystal. Heavy quasi-particle peaks can be observed in the vicinity of E_F, which are mainly originated from the hybridization between the 5f electrons and conduction electrons.

6) The successful preparation of high-quality USb_2 film provides an experimental platform for studying the influence of dimension regulation on U-based compounds by adjusting the film thickness and a powerful approach to deepen understanding of the heavy fermion systems in the future.

References

1 Kasuya T. *Progress of Theoretical Physics*[J], 1956, 16(1): 658

2 Mathur N D, Grosche F M, Julian S R *et al. Nature*[J], 1998, 394: 539

3 Chen Q Y, Luo X B, Xie D H *et al. Physical Review Letters*[J], 2019, 123(10): 5 106 402

4 Curro N J, Caldwell T, Bauer E D *et al. Nature*[J], 2005, 434: 4622

5 Imai H, Obara K, Diamond P J *et al. Nature*[J], 2002, 417: 4831

6 Kuroda K, Ochi M, Suzuki H S *et al. Physical Review Letters*[J], 2018, 120(8): 8 086 402

7 Fujimori S, Takeda Y, Okane T *et al. Journal of the Physical Society of Japan*[J], 2016, 85(6): 33 062 001

8 Jeffries J R, Stillwell R L, Weir S T *et al. Physical Review B: Condensed Matter*[J], 2016, 93(18): 7 184 406

9 Stillwell R L, Liu I L, Harrison N *et al. Physical Review B: Condensed Matter*[J], 2017, 95(1): 8 014 414

10 Ding Z F, Zhang J, Tan C *et al. Physical Review B: Condensed Matter*[J], 2019, 99(3): 6 035 136

11 Aoki D, Wisniewski P, Miyake K *et al. Journal of the Physical Society of Japan*[J], 1999, 68(7): 42 182

12 Wawryk R. *Philosophical Magazine*[J], 2006, 86(12): 131 775

13 Durakiewicz T, Riseborough P S, Olson C G *et al. Europhysics Letters*[J], 2008, 84(3): 637 003

14 Durakiewicz T, Riseborough P, Meng J Q. *Journal of Electron Spectroscopy and Related Phenomena*[J], 2014, 194: 423

15 Stewart G R. *Reviews of Modern Physics*[J], 2011, 83(4): 641 589

16 Hecht D S, Hu L, Irvin G. *Advanced Materials*[J], 2011, 23(13): 311 482

17 Damascelli A, Hussain Z, Shen Z X. *Reviews of Modern Physics* [J], 2003, 75(2): 69 473

18 Ji X Y, Chen Q Y, Lai X C *et al. Science China Physics, Mechanics & Astronomy*[J], 2020, 63(6): 6 267 411

19 Chen Q Y, Feng W, Xie D H *et al. Physical Review B: Condensed Matter*[J], 2018, 97(15): 7 155 155

20 Zhu X G, Liu Y, Zhao Y W *et al. npj Quantum Materials*[J], 2020, 5(1): 947

21 Wu Y, Fang Y, Li P *et al. Nature Communications*[J], 2021, 12(1): 72 520

22 Shimozawa M, Goh S K, Shibauchi T *et al. Reports on Progress in Physics*[J], 2016, 79(7): 21 074 503

23 Chatterjee S, Ruf J P, Wei H I *et al. Nature Communications*[J], 2017, 8(1): 7852

24 Berbil-Bautista L, Hänke T, Getzlaff M *et al. Physical Review B: Condensed Matter*[J], 2004, 70(11): 4 113 401

25 Chen Q Y, Tan S Y, Feng W *et al. Chinese Physics B*[J], 2019, 28(7): 5 077 404

26 Huth M, Kaldowski A, Hessert J *et al. Solid State Communications*[J], 1993, 87(12): 41 133

27 Jourdan M, Huth M, Adrian H. *Nature*[J], 1999, 398: 347

28 Shimozawa M, Goh S K, Endo R *et al. Physical Review Letters* [J], 2014, 112(15): 5 156 404

29 Bakhtizin R Z, Hashizume T, Xue Q K *et al. Physics-Uspekhi*[J], 1997, 40(11): 131 175

30 Cheng P, Song C, Zhang T *et al. Physical Review Letters*[J], 2010, 105(7): 4 076 801

31 Song C L, Wang Y L, Jiang Y P *et al. Physical Review B: Condensed Matter*[J], 2011, 84(2): 4 020 503

32 Chiotti P. *Bulletin of Alloy Phase Diagrams*[J], 1980, 1(2): 2109

33 Chang K, Liu J W, Lin H C *et al. Science*[J], 2016, 353(6296): 5274

34 Beaux M F, Durakiewicz T, Moreschini L *et al. Journal of Electron Spectroscopy and Related Phenomena*[J], 2011, 184(8): 8517

石墨烯/6H-SiC(0001)表面高质量USb_2薄膜的制备和表征

王西洋，郝群庆，张　云，潘启发，陈秋云，冯　卫，王永欢，朱燮刚，罗丽珠，赖新春，刘　琴，谭世勇

(表面物理与化学重点实验室，四川 绵阳 621908)

摘　要：重费米子体系可以通过维度等调控手段来展现出丰富而有吸引力的量子基态。首次通过分子束外延技术在石墨烯/6H-SiC（0001）衬底成功制备了高质量的USb_2薄膜。结合反射式高能电子衍射、X射线衍射、电输运和X射线光电子能谱测量，证明了所制备的USb_2薄膜是高质量的单晶薄膜。此外，利用扫描隧道显微镜和角分辨光电子能谱对USb_2薄膜的表面形貌、原子结构和能带结构进行了表征。结果显示，生长的USb_2薄膜的表面原子结构、电输运性质和能带结构与块体USb_2单晶相似。最后，高质量USb_2薄膜的成功制备和表征为未来通过生长理想厚度的超薄膜在低维铀基重费米子系统中探索奇妙性能提供了宝贵的实验经验。

关键词：USb_2薄膜；扫描隧道显微镜；角分辨光电子能谱；电子结构

作者简介：王西洋，男，1998年生，硕士，表面物理与化学重点实验室，四川 绵阳 621908，E-mail：15927186131@163.com