数理物質科学研究科　博士論文要約

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博士論文題目　Synthesis and Field Emission Properties of Transition Metal Carbide Nanowire

（遷移金属炭化物ナノワイヤーの合成と電界放出に関する研究）

1. Introduction

The electron source is the electron beam generator within electron gun similar to the light generator for microscopes. Nowadays, the functionality of electron source has been widely applied in a broad range of electron beam instruments including electron microscopy, electron lithography etc. Among of these applications, the performance of electron microscopies and electron lithography strongly associated with the fundamental properties of electron sources. Ideally, the electron source should be bright, stable and the energy spread of the electron beam should be as small as possible to meet the requirement for the high-resolution application. Depending on the mechanism of generating electron beam, there are three different kind of electron sources which are commonly used in electron beam instruments: thermionic emitter (TE), Schottky emission source and cold field emission emitter (CFE). Among of these candidates, the CFE is expected to provide electron beam with highest brightness and lowest energy spread so that it is consider having great potential for high resolution application.

One-dimensional materials with high aspect ratio and small area are believed to be optimal structures for the CFE due to their outstanding geometry, which could lead to low turn-on voltage and high brightness of CFE. Meanwhile, the materials with low work function such as transition metal carbides, nitride and borides have been widely investigated because these materials are believed to offer higher brightness, lower energy spread and lower turn on voltage for CFE as well. Among of these materials, the higher mechanical property and melting point of transition metal carbide provide it a better resistance to structure fracture caused by ion sputtering and high temperature induced by joule heating effect during field emission process. Thus, the transition metal carbide nanowire should be an attractive field emission material for CFE.

In this thesis, we reported the synthesis of transition metal carbides including HfC, and ZrC by chemical vapor deposition (CVD) based on vapor-liquid-solid mechanism (VLS). The parameters, which might affect the growth of nanowire were investigated. The field emission properties of both materials were evaluated. Due to the low work function and outstanding geometry of nanowire materials, high field enhancement factor and field emission current density were obtained for the CFE. Furthermore, to improve the stability of ZrC nanowire CFE, ZrC nanowire with inert coating was prepared, an enhanced field emission current stability was achieved with the surface processing.

2. Growth and Field-Emission of Single-Crystalline Hafnium Carbide Nanowire

Hafnium carbide (HfC), a transition metal compound with attractive properties including outstanding mechanical strength, high melting point (3900 °C), and low work function, has been considered as a promising material for field emission applications. The field emisison properties of HfC have investigated widely by preparing an electrochemical etched HfC CFE from bulk HfC. It has been showed that the HfC CFE can be operated under a wide range of temperature, electric field, and vacuum. The high mechanical strength of HfC makes it more resistant to the irreversible structural fracture caused by ion bombardment while the high melting point enables it to be flash cleaned at high temperature without degradation. On the other hands, 1D materials such as nanowire provide CFE a lower turn on voltage and higher brightness. Thus, it is worth conbining the merits of them and to improve the performance of HfC CFE.

In general, the field emission performance of a HfC nanowire depends strongly on the crystallinity and morphology of the sample. Therefore, it is necessary to prepare samples with optimal crystallinity and morphology. The chemical vapor deposition (CVD) is one of the common methods to prepare nanowire with high crystallinity. To synthesis HfC nanowire using CVD, the key parameters including temperature, content of $HfCl_4$, flow of CH_4, for HfC synthesis can greatly affect the formation and growth of a HfC nanowire. Therefore, it is necessary to figure out the influence of those factors in order to prepare HfC nanowires with a uniform morphology, high aspect ratio, high purity, and high crystallinity.

In this study we investigated the synthesis parameters, including amount of $HfCl_4$, synthesis temperature, and flow rate of CH_4 on the resultant morphology of the HfC nanowires. Our results suggested that lower $HfCl_4$ (< 1 g) and higher temperature (>1250 ℃) could reduce the formation of kinking and benefit the growth of collimated HfC nanowire. On the other hand, increasing flow rate of CH_4 could promote the growth of HfC nanowires and result in dense growth of single-crystalline HfC nanowires with high aspect ratio.

The field-emission properties of a HfC nanowire was also measured and presented in this work. A basic requirement for electron source is that the electron beam must be localized at tip apex of the emitter. However, the as-prepared nanowire inevitably has some protrusion or adsorbates on the tip. To address the problem, field evaporation was applied to the HfC nanowire to clean and reshape HfC nanowire. After field evaporation, clean HfC nanowire with sharpen tip was prepared. The electron beam was focused at tip apex due to the unique geometry of sharpen nanowire. A high field enhancement factor of 5.57×10^6 m^{-1} was obtained in the field emission measurement, indicating that the HfC nanowire CFE is capable to be operated at a lower applied voltage comparing to conventional cone shape HfC. Indeed, A field emission current of 207 nA with high density of 6.60 A/m^2 was observed from HfC nanowire at low applied voltage of 790 V. Our works suggested that HfC nanowire could be considered as potential materials for CFE.

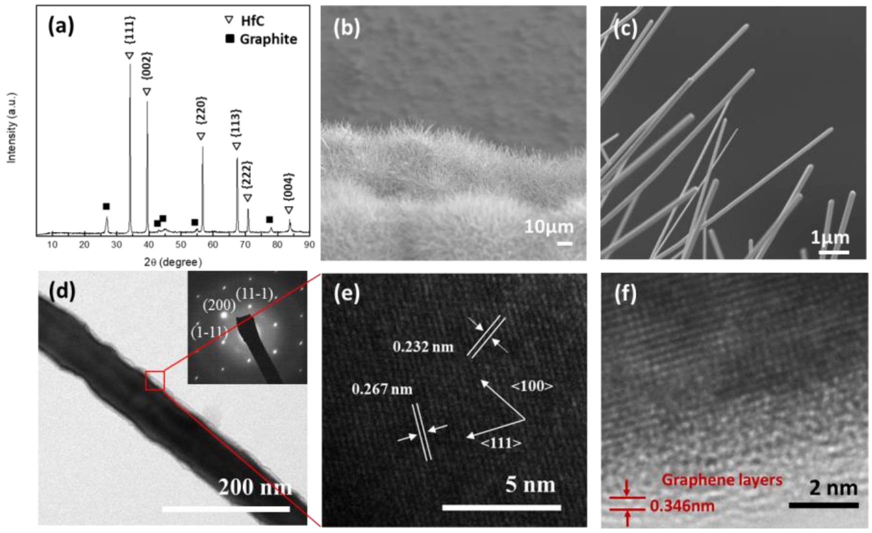

Figure 1 (a) X-ray diffractogram of as prepared sample showing Bragg reflections due to HfC and graphite substrate. (b-c) SEM images of HfC nanowires showing homogeneous growth. (d-f) TEM images of a HfC nanowire grown in <100> direction

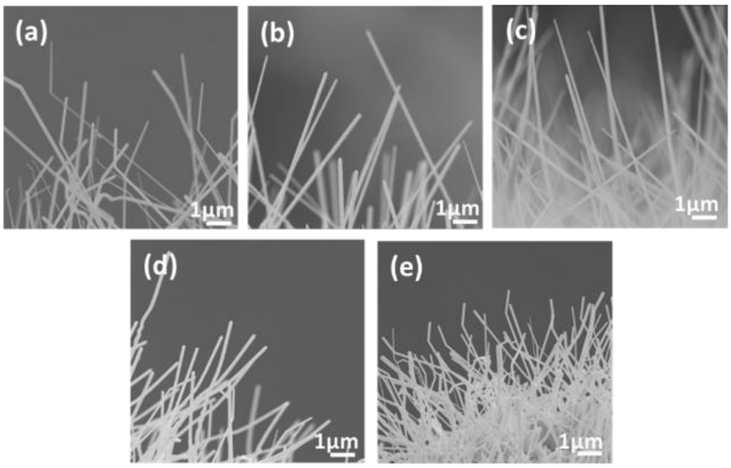

Figure 2 (a) SEM image of HfC nanowires synthesized with 1.00 g of $HfCl_4$ at 1280 °C. HfC nanowires showed kinked growth. (b) SEM image of HfC nanowires synthesized with 0.85 g of $HfCl_4$ at 1280 °C. HfC are free of kinks. (c) HfC nanowires synthesized with 0.70 g of $HfCl_4$ at 1280 °C. HfC nanowires are free of kinks. (d) HfC nanowires synthesized with 0.70 g $HfCl_4$ at 1230 °C. HfC nanowires showed kinked growth. (e) HfC synthesized with 0.70 g of $HfCl_4$ at 1180 °C. HfC nanowires showed kinked growth.

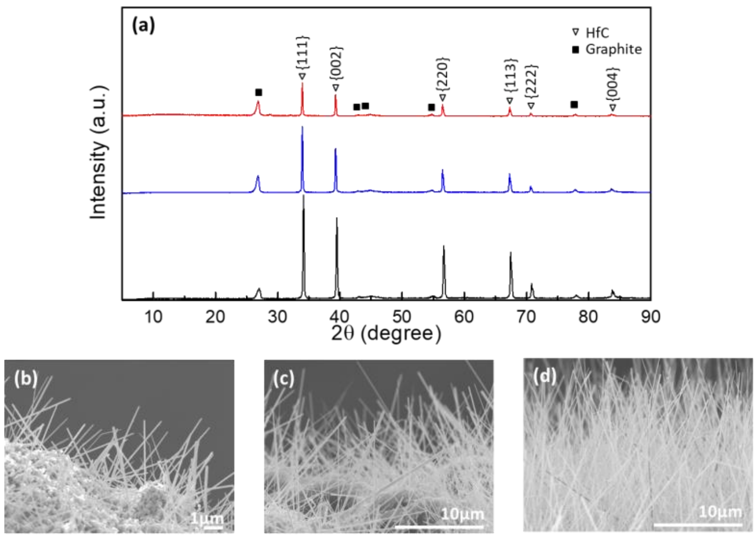

Figure 3 (a) XRD of HfC nanowires synthesized by different CH_4 flow rates. (b) SEM image of HfC nanowires synthesized at 20 ml/min of CH_4. (c) HfC nanowires synthesized at 60 ml/min of CH_4. (d) HfC nanowires synthesized by 100 ml/min CH_4.

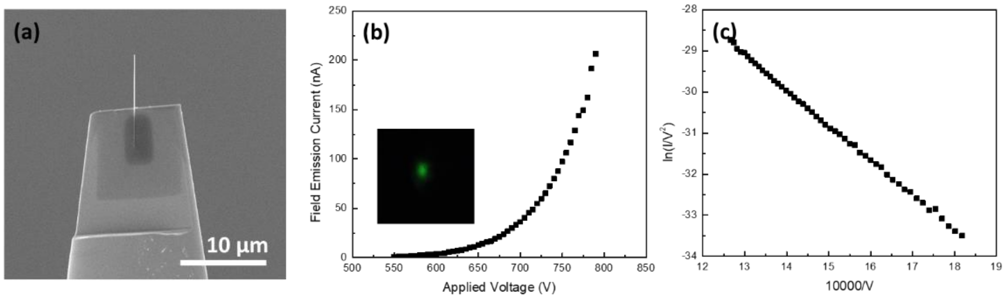

Figure 4 (a) SEM image of an assembled HfC nanowire CFE. (b) I-V curve. The inset is the field emission pattern of the emitter. (c) F-N plot of the HfC nanowire CFE.

3. Synthesis and Field-Emission of Single-Crystalline Hafnium Carbide Nanowire

Zirconium carbide (ZrC) is another kind of promising transition metal carbide with many attractive properties including low work function, high mechanical strength, and excellent chemical stability that make it a promising material for field emission applications. The work function of ZrC is also about 1 eV lower than conventional metal emitter such as W and Mo. The low work function of a field emission material is expected to provide an advantage for high resolution imaging and spectroscopy applications. Similar to the HfC, the excellent mechanical strength of ZrC could benefit the structural integrity of the CFE due to the improved resistance to ion sputtering. The high melting point enables it to withstand the high temperature induced by large emission current or thermal flashing without degradation comparing to the other field emission materials. Moreover, a lower cost of ZrC comparing to HfC provide it a greater potential in industry application. Because of these advantages, the field emission properties of ZrC have been investigated extensively.

To prepare a ZrC electron source, a usual method is to shape the ZrC crystal into a conical tip with a radius of a few hundred nanometers by electrochemical etching. However, the relatively large radius and emission area of such conical emitters usually require higher turn-on voltages and reduce the brightness of the CFE, limiting the effective application.

Based on our previous work, one-dimensional (1-D) material with a high aspect ratio and sharp tip is a more favorable structure as a CFE. The unique geometry of 1-D materials can enhance the local electric field at the tip and allows field emission to occur at a lower applied voltage. In addition, the smaller field emission area of a nanowire is expected to benefit the emission brightness. However, the field emission properties of a single ZrC nanowire have not been investigated to the best of our knowledge, therefore it is worth to evaluate the field emission performance of ZrC nanowire.

In this study we reported the synthesis of ZrC nanowire using CVD and the field emission performance of a single-crystalline ZrC nanowire. Field evaporation was applied to the ZrC nanowire to remove and sharpen the tip. A favorable electron beam, which localized at the tip apex was obtained after field evaporation. The high aspect ratio of nanowire provides a high field enhancement factor of 8.23×10^{6} m^{-1} for CFE. A field emission current of 194 nA was obtained at low applied voltage of 555 V, which is about 3000 V lower than the traditional cone shaped ZrC CFE. The corresponding current density is calculated as high as 6.92×10^{10} A/m^{2} at a low applied voltage of 555 V, which is attributed to a combination of meriteous factors including a low work function, a high field enhancement factor, and a small emission area of the ZrC nanowire CFE.

These characteristic features suggested that the ZrC nanowire is a promising structure for field emission point source applications.

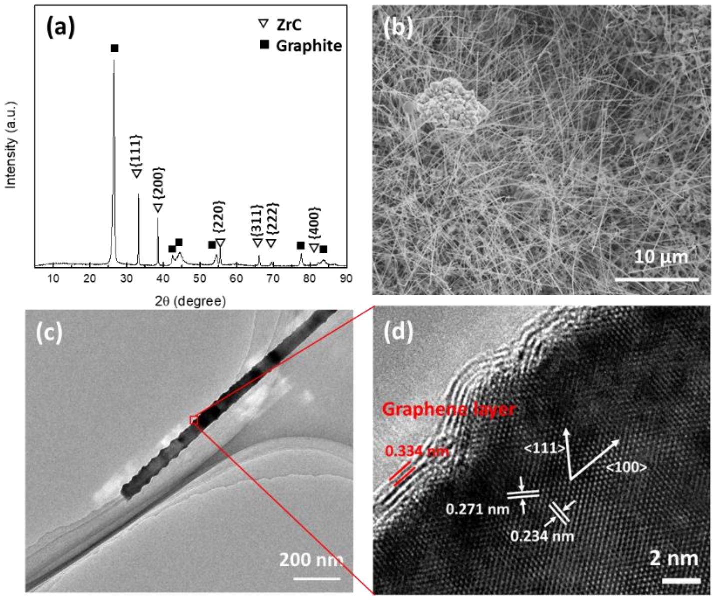

Figure 5 (a) The XRD of ZrC nanowire (b) The SEM image of ZrC nanowire. (c) The TEM of ZrC nanowire. (d) The HRTEM image of ZrC nanowire

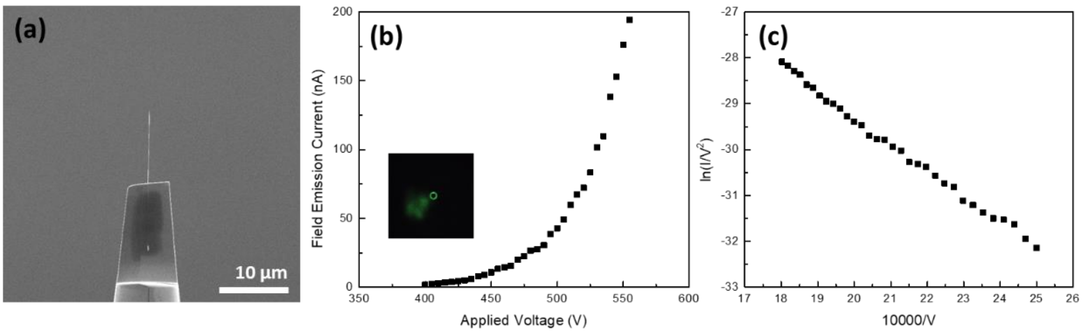

Figure 6 (a) SEM image of an assembled ZrC nanowire CFE. (b) I-V curve of ZrC nanowire. The inset is the field emission pattern of the emitter. (c) F-N plot of the HfC nanowire CFE.

4. Enhanced Field Emission Stability of ZrC Nanowire by Applying Inert Coating

The potential of using single ZrC nanowire as CFE has been reported in previous work. Comparing to the electrochemically etched ZrC CFE, the ZrC nanowire CFE exhibit high current density at low applied voltage due to excellent geometry. The results indicated that ZrC nanowire is a potential material for field emission application. However, although the ZrC nanowire CFE had excellent field emission performance, the field emission stability was still far below the requirement for practical application. The flicker noise and the decay of field emission current caused by the adsorption and desorption of residual gas molecule was a serious problem for ZrC nanowire CFE and greatly limited its applications. To reduce the influence of residual gas molecule, a typical approach is coating the field emission materials with an inert surface such as oxide or carbon layer. This method has been demonstrated to be effective in the other transition metal oxide materials.

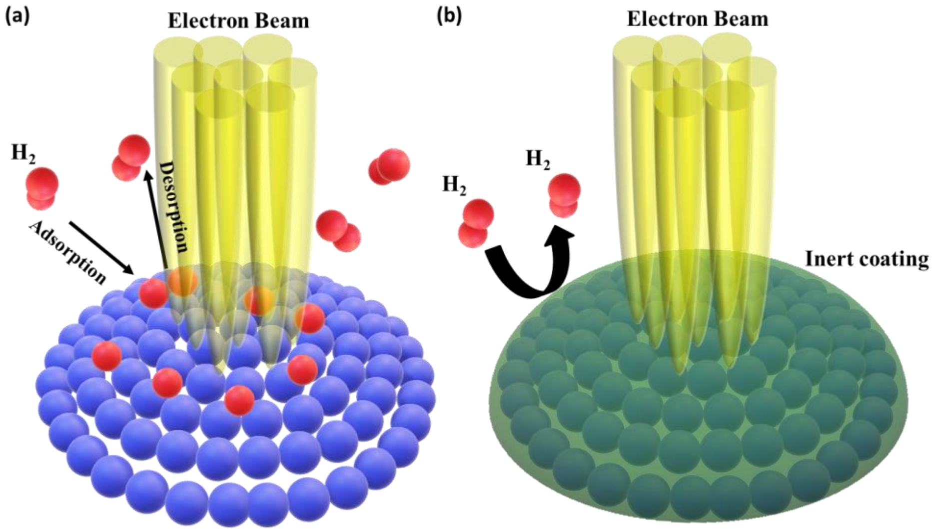

Figure 7 (a)The mechanism of flicker noise and decay of field emission current. (b) The approach to reduce the influence of residual gas molecule.

To address the problem of poor field emission stability and further improve the field emission performance of ZrC nanowire CFE, it is worth to deposit a stable outmost layer on the surface of ZrC nanowire. In this study, we evaluated the field emission stability of few layers of graphene coated ZrC and oxidized ZrC. The few layers of graphene were synthesized during VLS growth of ZrC nanowire and were attached on the as-grown ZrC nanowire. The oxidized ZrC nanowire was prepared by heating ZrC nanowire in oxygen atmosphere. The field emission stability of ZrC nanowire with inert coating was presented in this work. In both case, field emission current with noise below 2% was obtained, which suggested that such kind of inert surface greatly reduce the influence of residual gas molecule leading to better field emission stability of ZrC nanowire. In addition, by oxidizing ZrC nanowire, the turn on voltage of ZrC was noticed to be significantly reduced, which may result from the reduction of work function. Our results indicated that ZrC nanowire inert coating has exciting field emission stability and better resistance to lower vacuum level.