The structure and phase change of a molybdenum grid coated with silicon and carbon composite thin films annealed at high temperature

J. Wang[a,b], X.M. Wu[a,*], L.J. Zhuge[a,c]

[a]*Department of Physics, Suzhou University, Suzhou 215006, China*
[b]*Department of Electronics and Information Engineering, Suzhou University, Suzhou 215006, China*
[c]*Analysis and Testing Center, Suzhou University, Suzhou 215123, China*

Abstract

Si–C composite thin films were deposited onto molybdenum substrates by radio-frequency magnetron sputtering. In order to simulate the working conditions of a grid contaminated by the active electron emission substance BaO from the hot cathode of a pulse-controlled grid travelling-wave tubes (TWTs), BaO layers were chemically deposited on the surface of the Si–C films. The structure and phase changes of BaO/Si–C/Mo systems were investigated using Raman scattering and XRD analysis after annealing at temperatures from 973 to 1273 K. The results show that high temperature annealing leaves only the high work function materials, SiC (about 4.4 eV) and SiO$_2$ (about 3.1 eV), remaining on the surface. The results are discussed in terms of chemical reactions believed to occur during annealing and the importance of these for electron suppression from grids in working TWT devices.
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1. Introduction

Pulse-controlled grid traveling-wave tubes (TWTs) are widely used in the space and defence radar systems for navigation and direction of aircraft, satellites, and guided missiles. TWT-based systems have the advantages of high gain, high power, a wide operational frequency band and, in addition, they have relatively small volume and light weight with a good record of reliability [1]. In order to operate at higher frequencies and powers, the tubes use grids that are very close to cathode, which operates at a temperature in the range 1250–1300 K. High electron emission is produced by the activation of the hot cathode that creates a low work function BaO or Ba surface [2]. Thus, the neighboring grid is heated to about 1050–1250 K depending on its proximity to the cathode, and this in turn

can lead to hot electron emission from the grid surface. The situation is aggravated by the fact that BaO or Ba can be evaporated onto the grid surface from hot cathode, thus lowering the grid surface work function and increasing the grid emission current further. This ''grid emission'' phenomenon can destroy the grid cut-off characteristics of the tube and render it effectively unusable [3].

Recently, Liu et al. [4] have found that a graphite carbon film is suitable for Mo grid coating and grid emission can be effectively suppressed. The other material used in non-emitting grids is hafnium [5,6]. Silicon carbide (SiC) has a wide-band gap, high saturated electron velocity, high electrical breakdown field, high thermal conductivity and high surface hardness and can be applied as a corrosion-resistant surface coating. These properties make this material suitable for high-power, high-frequency and high-temperature applications [7] and suggest its use as a possible candidate for non-emitting grids.

In this paper, we describe the deposition of silicon and carbon composite thin films on the surface of a Mo grid

*Corresponding author. Tel.: +86 512 6511 2511;
fax: +86 512 6511 1907.

E-mail address: xmwu@suda.edu.cn (X.M. Wu).

using RF-magnetron sputtering. The structure and phase changes of BaO/Si–C/Mo systems were investigated following annealing in vacuum over the temperature range 973–1273 K. The suppression mechanism of electron emission from the grid coated with silicon and carbon composite thin films is discussed.

2. Experimental

Silicon and carbon composite thin films were deposited on the Mo substrates at a substrate temperature of 673 K by radio-frequency magnetron sputtering using a silicon and carbon composite target. Mo substrates were cleaned in acetone and alcohol followed by sulphuric and nitric acids, rinsed with deionized water, dried in a flux of N_2 and immediately placed into the sputtering chamber. The chamber was evacuated to 6×10^{-4} Pa and argon gas was then introduced through a mass-flow controller. Sputtering was performed at an argon pressure of 1.0 Pa and RF power of 200 W producing growth rate of approximately 9 nm/min. The thickness of the as-deposited thin films was about 500 nm controlled by the sputtering time.

The mechanism of grid electron emission was investigated by simulating the working conditions of a grid contaminated by BaO by activation of the hot cathode. BaO layers were deposited on the Si–C/Mo systems by a chemical method. The samples were immersed in $Ba(NO_3)_2$ saturated solutions (about 8.7 g $Ba(NO_3)_2$ powder was dissolved in 100 cm^3 water at 293 K) for 7 h, and were then annealed at 973 K for 1 h to form BaO on the surface of Si–C/Mo systems. Finally, the samples were annealed under vacuum ($\sim 10^{-4}$ Pa) at different temperatures for 1 h to investigate the structure and phase changes of BaO/Si–C/Mo systems.

The compositional and phase changes of BaO/Si–C/Mo systems were studied by X-ray diffraction (XRD) using Cu K_α radiation performed on a Rigaku D/Max-3C (Cu K_α, $\lambda = 0.15406$ nm). Raman spectra were obtained in the back-scattering configuration between 300 and 2000 cm^{-1} with a JY-H800 instrument using an argon ion laser at a wavelength of 632.81 nm. All the measurements were conducted at room temperature.

3. Results and discussions

Raman scattering measurement can provide information concerning Si–C, Si–Si, C–C bonds and recrystallization. The Raman spectra for the samples annealed at different temperatures are presented in Fig. 1. After annealing at 973 K for 1 h, the broad asymmetric peak at 420–520 cm^{-1} can be attributed to Si–Si TO mode (480 cm^{-1}) [8] and SiC vibration band (around 500 cm^{-1}) [9]. The peaks centered at 1332 and 1600 cm^{-1} are related to the TO mode of diamond and the graphite structure of carbon, respectively [10]. With the increase in annealing temperature up to 1273 K, it can be seen that the sharp peaks located at 791 and 910 cm^{-1} are assigned to the SiC bonding configura-
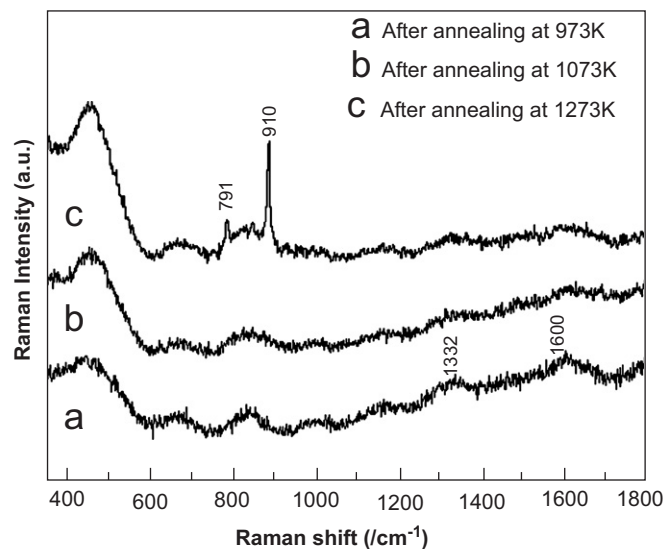

Fig. 1. Raman spectra of the Si–C/Mo after immersing in Ba $(NO_3)_2$ saturated solutions: (a) after annealing at 973 K, (b) after annealing at 1073 K, and (c) after annealing at 1273 K.
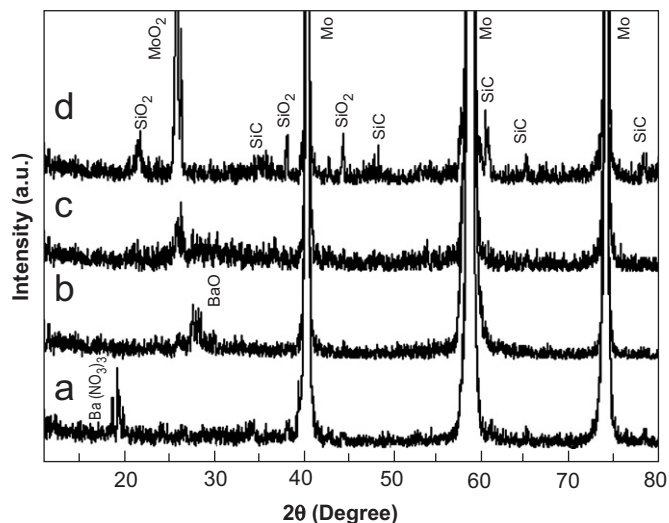

Fig. 2. XRD spectra of the Si–C/Mo after immersing in Ba $(NO_3)_2$ saturated solutions: (a) as-deposited, (b) after annealing at 973 K, (c) after annealing at 1073 K, and (d) after annealing at 1273 K.

tions with 4H–SiC structures [11] and the SiO_2 matrix [12], respectively. Moreover, with the increase of annealing temperature, the lack of C–C bands at 1300–1600 cm^{-1} suggests that the carbon atoms are gradually bonded to silicon atoms to form SiC.

Fig. 2 shows results for BaO coated samples. $Ba(NO_3)_2$ peaks are found in the XRD spectra before annealing and, after annealing at a temperature of 973 K for 1 h, the $Ba(NO_3)_2$ peaks disappear and a BaO peak appears. At $T_a = 1073$ K, peaks of SiO_2 and SiC appear while the intensity of the BaO peak becomes weak as compared with that of the sample annealed at 973 K. As the annealing