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Temporal evolution of ion fragment production from methylsilane by a hot tungsten wire

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Temporal evolution of ion fragment production from gaseous methylsilane in contact with a hot tungsten wire was measured with a use of a low-energy mass analyzed ion beam system. The mechanisms of molecular fragmentation in the system are similar to those for typical catalytic chemical vapor deposition processes. The fragmentation rates vary during the process due to surface modification of the tungsten wire. The extent of surface modification depends on the tungsten temperature. When the tungsten temperature was set to 1940 °C, ion fragments were produced initially but the production terminated about 1 h after the start of the experiment. The termination of ion production seems to be caused by the formation of a thick 3*C*-SiC layer on the tungsten surface, which was identified by x-ray diffraction measurement. When the tungsten temperature was set to 2220 °C, ion fragment production continued at least for 8 h. In this case the layer of deposited compounds, which mainly consist of WC, W_2C, C, and 4*H*-SiC, was relatively thin. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2364050]

Catalytic chemical vapor deposition (Cat-CVD) (which is also known as hot wire CVD) processes have attracted much attention as means of creating various materials.[1–5] In Cat-CVD processes, the source gas is fragmented into highly reactive radicals and ions through some surface reactions on the catalyzer (e.g., hot tungsten wire). However, basic characteristics of the fragmentation processes have not been well understood to date.

Recently we have proposed a method for the characterization of such fragment ions. For example, we reported basic characteristics of fragment ions produced from methylsilane (H_3Si-CH_3) with a hot tungsten wire in a recent paper.[6] The mass numbers of the main fragment ions from methylsilane were identified to be 15, 29, 44, 1, 2, and 3. These fragment ions mainly correspond to CH_3^+, SiH^+, $SiCH_4^+$, and hydrogen ions (H_1^+, H_2^+, H_3^+). The energy spreads of all measured ions were small and the produced ions gained virtually no kinetic energy in the ionization process. These observations indicate that the fragment ions were generated by surface ionization on the hot tungsten surface. In addition, some compounds were observed to be formed on the tungsten wire surface during the experiments.

In general the fragmentation rates change in time during the Cat-CVD processes due to surface modification of the catalyzer. However, temporal evolution of the ion production rates has not been measured for the methylsilane reactions considered here. The goal of this work is to present the time variation of fragmentation rates and their relations with the catalyzer temperature and surface conditions. In this work, time evolution of CH_3^+, SiH^+, and $SiCH_4^+$ ion currents generated from methylsilane is reported. Identification of compounds deposited on the tungsten surface and dependence of their characteristics on the tungsten temperature are also presented.

The experiments were carried out in a low-energy mass analyzed ion beam system with a Freeman-type ion source. The beam system consists of the ion source together with an extraction electrode, a magnetic-field-based mass selector, a Faraday cup, and a process chamber (i.e., a chamber where the ion beams may be used for some material processes).[7] The ion source consists of a stainless chamber (25.4 mm in diameter, 50.8 mm in length) and a tungsten wire (2 mm in diameter). The configuration of the ion source is similar to that of a typical Cat-CVD apparatus.[6] First we supply an electric current ($\leqslant 150$ A) to the tungsten wire. Next a methylsilane gas [0.8 SCCM (SCCM denotes cubic centimeter per minute at STP)] is supplied to the ion source chamber through the gas feed tube. Fragment ions produced in the ion source chamber are extracted by a high voltage applied to the extraction electrode (at −25 kV in this experiment). The ion beam intensity for each ion fragment species selected by the mass selector can be measured by the Faraday cup installed

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TABLE I. Experimental conditions: the tungsten wire currents, duration of the experiments, tungsten temperatures evaluated from the electrical resistance, and wire diameters after the experiments.

	Wire current (A)	Duration (h)	Temperature (°C)	Diameter (mm)
(a)	80	8	1220	2.06
(b)	100	1	1610	2.11
(c)	120	4.5	1860	2.94
(d)	130	4.5	1940	2.79
(e)	150	8	2220	2.19

just behind the mass selector. The gas pressure in the region between the ion source and the Faraday cup during the experiment is about 10^{-3} Pa. The mean free path is several meters, which is larger than the device size. Therefore, ion-molecule reactions can be neglected during the transportation of the ions from the ion source to the Faraday cup.

The experiments were performed in the five conditions (a)–(e) given in Table I. The wire current was kept nearly constant during each experiment. The temperatures listed in Table I are those of the tungsten wires evaluated from their electrical resistance before they were exposed to the methylsilane gas in the experiments. The wire temperatures given in Table I were confirmed to agree approximately with those measured by a radiation thermometer (CHINO IR-CAQ2CS) in the previous experiments[6] although temporal evolution of the wire temperature during each experiment was not monitored. After the experiments (a)–(e), some compounds were deposited on the tungsten wire surface and the wire diameter, which was initially 1.99 mm, increased in some degree. The final wire diameters were measured by a micrometer after the experiments and their values are listed in Table I. In case (a), where the wire current was 80 A, the wire diameter increased only slightly (2.06 mm) and only a small amount of compounds was observed to be deposited on the wire surface. In cases (c) and (d) (120 and 130 A) the deposited compounds were sufficiently thick (2.94 and 2.79 mm). In case (e) (150 A), the increment of the wire diameter was small (2.19 m) compared with those in cases (c) and (d).

Figures 1(a)–1(c) show the time evolution of the three dominant fragment ion currents (CH_3^+, SiH^+, and $SiCH_4^+$) produced from methylsilane for two different tungsten wire currents, i.e., 130 and 150 A. In each figure, the vertical axis represents the current measured at the Faraday cup installed immediately behind the mass selector and the horizontal axis represents the duration of each experiment. The Faraday cup current is an indicator of the production rate of each ionic species. The measured currents in Figs. 1(a)–1(c) evolve in a similar manner for each tungsten temperature. When the tungsten wire current was 130 A (and the tungsten temperature was 1940 °C), the initial Faraday cup current was small and then increased gradually for the first 40 min. Then it decreased and eventually terminated at around 80 min. When the tungsten wire current was 150 A (2220 °C), the Faraday cup current was large in the beginning and decreased gradually for the first 60 min. For the next few hours, however, it decreases more slowly and, after about 330 min, it became almost time independent. On the other hand, fragment ions were hardly detected when the tungsten wire currents were smaller, i.e., 80, 100, and 120 A.

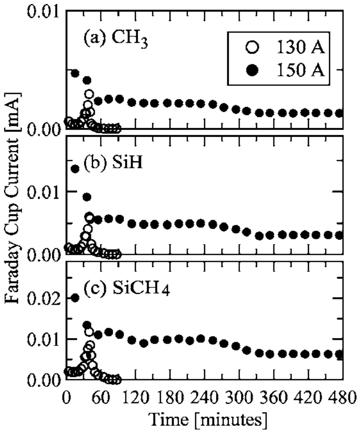

FIG. 1. Temporal evolution of Faraday cup ion currents for (a) CH_3^+, (b) SiH^+, and (c) $SiCH_4^+$ produced from methylsilane by a hot tungsten wire. The tungsten wire current is set to 130 or 150 A.

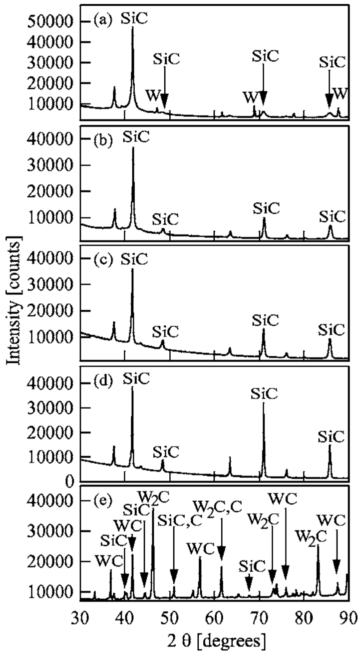

FIG. 2. The x-ray diffraction patterns ($\theta-2\theta$ method) of the compounds formed on the tungsten wire surface. The tungsten wire currents are (a) 80 A, (b) 100 A, (c) 120 A, (d) 130 A, and (e) 150 A.

The x-ray diffraction (XRD) measurements of the compounds deposited on the tungsten wires were made with an x-ray diffractometer (RIGAKU RINT2200) with radiation $K\alpha_1$ of Co ($\lambda = 1.788\ 92$ Å). Shown in Figs. 2(a)–2(e) are the XRD patterns of deposited compounds for the experiments (a)–(e) given in Table I, respectively. In Figs. 2(a)–2(e), the identified compounds corresponding to peaks in the XRD patterns are also shown. The XRD patterns of Figs. 2(a)–2(d) are similar and the main component of deposited material is silicon carbide (3*C*-SiC). Note that, in Fig. 2(a), peaks corresponding to tungsten (W) are also observed since the deposited compound was sufficiently thin, as indicated in Table I. In contrast to Figs. 2(a)–2(d), however, many peaks are seen in Fig. 2(e), which correspond to tungsten carbide (WC, W_2C), carbon (C), and SiC. In this case, the formation of

4*H*-SiC is observed instead of 3*C*-SiC because the tungsten wire temperature is relatively high.[8]

In summary, the temporal evolution of fragment ions produced from gaseous methylsilane by a hot tungsten wire was measured with the low-energy mass analyzed ion beam system. It has been found that when the tungsten temperature is lower than 1900 °C, fragment ions are hardly generated. In this case the methylsilane gas is adsorbed and 3*C*-SiC is formed on the wire surface. When the tungsten temperature is 1940 °C, fragment ions are generated initially but then their production ceases after some time probably because a thick 3*C*-SiC film is formed on the tungsten wire surface. When the tungsten temperature is as high as 2220 °C, however, the ion fragment production is maintained for an extended period. In this case, WC, W_2C, and C as well as 4*H*-SiC are also formed on the hot wire surface and the layer of deposited compounds is relatively thin. The presence of WC and W_2C is the evidence of the dissociation of methylsilane gas by reactions on the tungsten wire surface.

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