Fragment ions of methylsilane and dimethylsilane generated in tungsten-based catalytic chemical vapor deposition (Cat-CVD) processes

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Introduction

Recently Cat-CVD, which is also known as hot wire CVD, processes have attracted much attention as a method for the growth of semiconductor films, such as silicon carbide (SiC), amorphous Si, and polycrystalline-Si. Despite the widespread study of Cat-CVD applications, basic characteristics of fragment ions produced in such processes have not been well understood to date.

The goal of this work is to present a catalogue of fragment ions produced by Cat-CVD processes and to analyze their characteristics. Although, in actual Cat-CVD processes, charge-neutral radical species are believed to be dominant deposition precursors, measurements of charge-neutral species are beyond the scope of the present work. We believe that information on fragment ions produced by catalytic surface reactions facilitates our understanding of basic reaction mechanisms in Cat-CVD processes.

In our experiments, methylsilane or dimethylsilane gas is supplied to a hot tungsten wire in a chamber that we call the ion source. This ion source may be considered as a model chamber of Cat-CVD processes. In the ion source, the gas is broken down into ions and charge-neutral species due to the presence of a hot tungsten wire. Among these species, only ions are directly extracted from the chamber by an applied high voltage and sent to a magnetic-field-based mass selector. Then the selected ions are detected and their kinetic energies are measured. In this way, ions produced in the Cat-CVD model chamber are identified and characterized. Dependence of ionization rates on the tungsten wire temperature is also measured.

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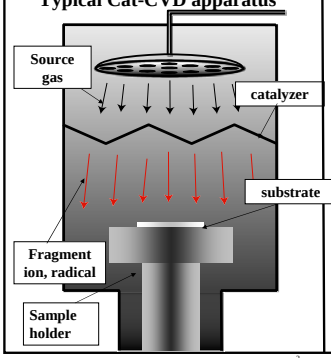
catalytic chemical vapor deposition (Cat-CVD)

Typical Cat-CVD apparatus



Cat-CVD process

Source gas is supplied to the process chamber

Source gas is fragmented into radicals and ions through surface reactions on the hot catalyzer

Growth of various functional semiconducting and insulating materials on the substrate

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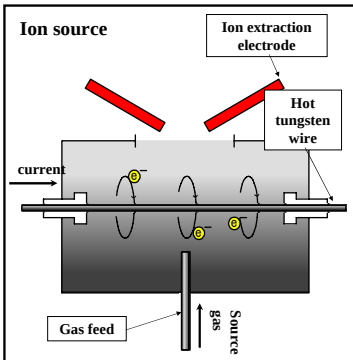
Fragment ions produced in ion source

Ion source



Production of fragment ion

Source gas is supplied through gas feed

the gas is broken down into ions and charge-neutral species due to the presence of a hot tungsten wire.

Among these species, only ions are directly extracted from the chamber by an applied high voltage and sent to a magnetic-field-based mass selector.

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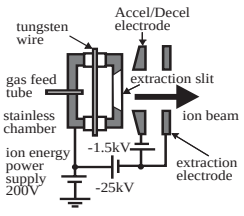
Ion source



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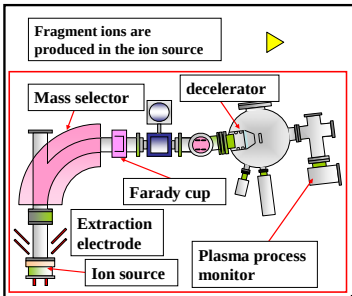
method of characterization for such fragment ions

Fragment ions are produced in the ion source



ions are extracted from the chamber by an applied high voltage (Extraction electrode)

Ions are analyzed by the magnetic-field-based mass selector.

The intensity of the mass analyzed ion beam can be measured by the Faraday cup

The ion beam is deflected for the removal of high energy neutrals and then is decelerated to the desired kinetic energy.

The beam quality can be examined by the plasma process monitor, which is a mass and energy detector.

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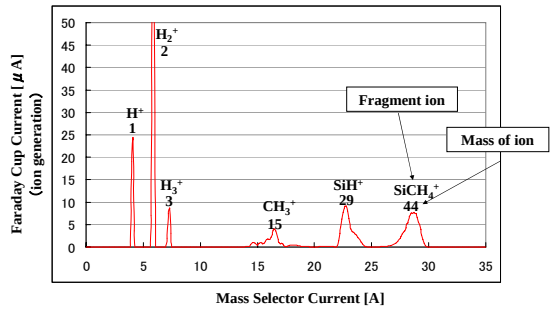
Fragment ion from methylsilane (SiH_3CH_3)

Catalyzer Temperature : about 2100℃



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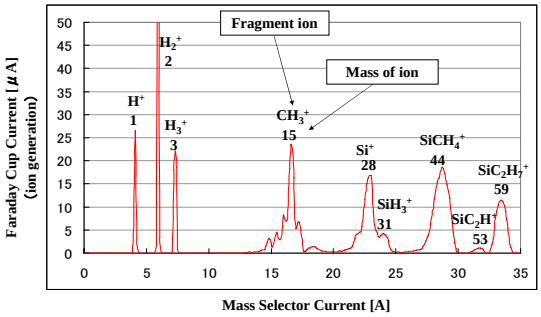
Fragment ion from methylsilane ($CH_3SiH_3CH_3$)

Catalyzer Temperature : about 2300℃



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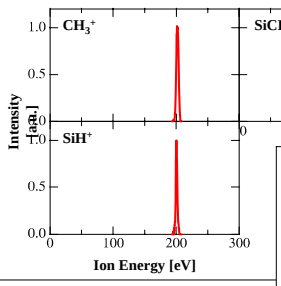
Energy distribution of fragment ions of dimethylsilane

Catalyzer temperature: about 2100℃



For each distribution, the peak energy is about 200 eV and the Full Width at Half Maximum (FWHM) is about 2-4 eV. The energy spreads of all measured ionic species are small, which indicates that, in actual methylsilane Cat-CVD processes, the produced ions are unlikely to cause any significant damage to the deposited films. The mean energy of 200 eV is the energy supplied for the transportation of ions to the detector.

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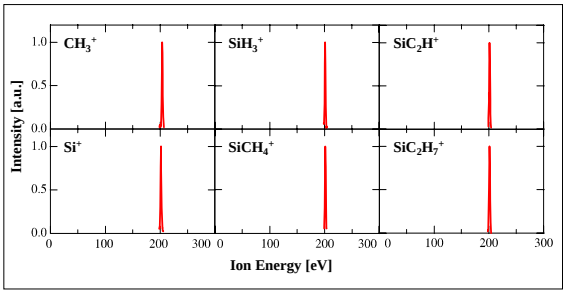
Energy distribution of fragment ions of dimethylsilane

Catalayzer temperature : about 2300℃



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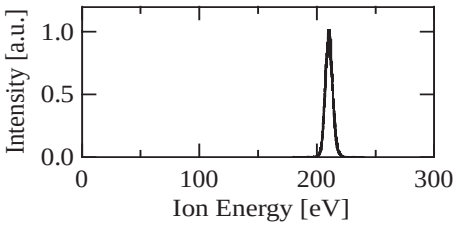
Energy distribution of Ar ions produced in the same ion source with Ar gas



The energy distributions of the fragment ions present a sharp contrast to those of noble gas ions such as Ne, Ar, Kr, and Xe. The FWHMs of energy distributions for such noble gas ions are typically in the range of 5-10 eV with mean kinetic energies of about 5-10 eV, as shown in the above fugure.

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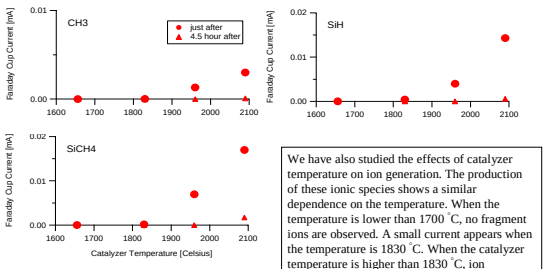
Effect of the catalyzer temperature on ion generation (methylsilane)



We have also studied the effects of catalyzer temperature on ion generation. The production of these ionic species shows a similar dependence on the temperature. When the temperature is lower than 1700 ˚C, no fragment ions are observed. A small current appears when the temperature is 1830 ˚C. When the catalyzer temperature is higher than 1830 ˚C, ion production increases significantly as the temperature becomes higher.

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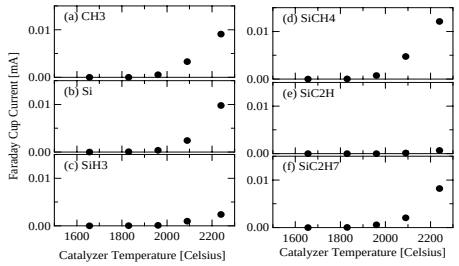
Effect of the catalyzer temperature on ion generation (dimethylsilane)



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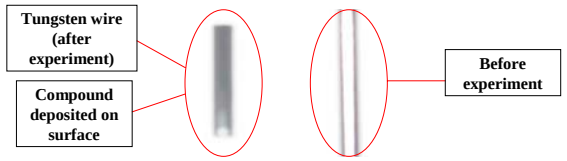
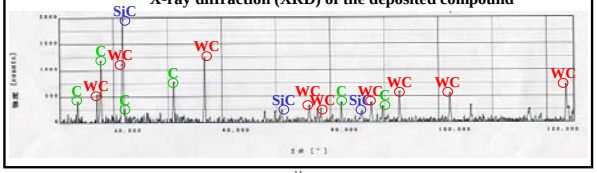
Deposited compound on tungsten surface (methylsilane)



X-ray diffraction (XRD) of the deposited compound



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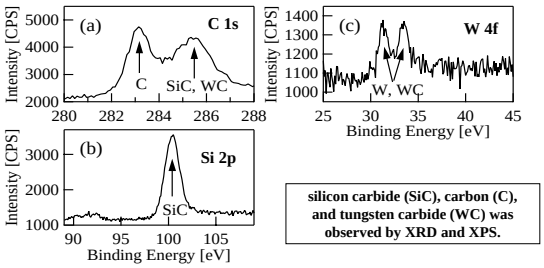
x-ray photoelectron spectroscopic measurement (XPS)



silicon carbide (SiC), carbon (C), and tungsten carbide (WC) was observed by XRD and XPS.

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Conclusion

Fragment ions produced from methylsilane and dimethylsilane with a hot tungsten wire are identified with the use of a low-energy mass analyzed ion beam system. The ion source may be considered as a model process chamber for Cat-CVD processes. It is found that the dominant fragment ions from methylsilane are H1+, H2+, CH3+, Si+, SiH+, SiCH4+ and those from dimethylsilane are H1+, H2+, CH3+, Si+, SiH3+, SiCH4+, SiC2H+ and SiC2H7+. The energy distributions of these ions show that their energy spreads (e.g., FWHMs) are small. This means that, in actual methylsilane and dimethylsilane Cat-CVD processes, ions produced in this process are unlikely to cause any significant damage to the deposited films. It is also found that ion generation rates strongly depend on the catalyzer temperature. Especially there is a threshold temperature of the tungsten wire, which is 1900 ˚C in the case of our ion source. The ion production rates decreased with time due to modification of the tungsten wire surface during the process. The x-ray diffraction and x-ray photoelectron spectroscopic measurements showed that silicon carbide, carbon, and tungsten carbide compounds were formed on the tungsten wire surface during the process.

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