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## 論文内容の要旨

A study of synchrotron radiation excited CVD (chemical vapor deposition) and etching of semiconductor surfaces was initiated about ten years ago. It has attracted considerable attention in the hope that this technique would provide us with unique features and advantages of using SR; (1) cleanliness of the process environment, (2) lowering of process temperatures, (3) material selectivity owing to strong absorption cross sections in the extreme ultraviolet region, and (4) finer machinability owing to the use of short wavelength light. At the early stage of the research unique phenomena were found concerning material selectivity and space selectivity in using SR as a light source. Despite the efforts which had been spent the reaction mechanisms were not clarified; even what nascent species that desorb from the surface as reaction products had not been identified. Although surface science aspects of thermal etching reactions have been accumulated, SR-excited etching was not well studied. It was the time when I started participating this research.

In the present thesis SR-excited etching reactions are mainly studied using two techniques; one is to measure the etch rate as a function of etchant gas pressure, wavelength of the irradiated light, type of etchant, and temperature for some semiconductor materials such as Si, $SiO_2$, and SiC as well as diamond and graphite and to discuss the mechanism of the etching reactions. Another approach is to detect desorbed species form the surface using electron bombardment ionization mass spectrometer detector and measure their velocity distributions from which some information about the dynamics of etching reactions involved has been obtained.

Using halogen containing gas of $SF_6$ as etchant, Si containing compounds of silicon, silicon dioxide and silicon carbide were etched by irradiating synchrotron light. From quantitative determination of the quantum yields for etching it has been found that surface photoexcitation process plays an important role in SR-excited etching. The etch rates are found to range from 0.2 to 0.02 Å mA/min depending on the type of etchant and wavelength of the extreme light used to stimulate etching reactions. For example, photoexcited etching of $SiO_2$ surface with $SF_6$ gas studied using undulator radiation at 143 and 251 Å. The $SF_6$ gas pressure and wavelength dependence of etch rates were measured for $SiO_2$ in the pressure region between 0.016 and 0.50 Torr. They have found that, at these wavelengths and in the pressure region studied, the etch rate is proportional to the amount of the light absorbed by one layer of surface moiety which is speculated to be $SiO_2$. In order to explain its quantum yields a reaction model for SR-excited etching that, as long as the fluorine radical concentration is high enough, the desorption reaction is induced with a unit

probability when one undulator photon is absorbed by the $SiO_2$ layer, has been proposed. The results are presented in the Chapter Ⅱ.

The next questions which he wanted to answer were what kinds of nascent species are desorbed from the fluorinated silicon surface, how much energy is partitioned to the translational motion of the desorbing products, and how they are affected by shining SR on the sample surface. Therefore he decided to detect the desorbed species from the surface in situ in SR-excited etching reaction. Though the major desorbed species of etching are expected to be neutral, they had not been detected in situ SR excited etching reaction because of the low intensity level expected. Carefully examining the sensitivity of available neutral detectors and estimated rates of SR-excited etching reaction, he has constructed an apparatus which enables them to measure the velocity distributions of the desorbed species formed in the SR-excited etching reaction of Si with halogen containing gases. The neutral desorbed species from the surface in the etching reaction of silicon have been identified from the measurements of their velocity distribution using a time-of-flight(TOF) technique combined with an electron bombardment ionization mass spectrometry (EBIMS). The major ion masses for the desorbed product species are $SiF_3^+$ and $SiF^+$ when the SR light with photon energies ranging from 50 to 500 eV is shone on the Si surface in $XeF_2$ atmosphere. The parent masses for the ion mass of $SiF_3^+$ are considered to be $SiF_3$ and/or $SiF_4$. In this case two components have been observed in the TOF spectra; a fast and a slow component. The slow component is fitted to a Maxwell-Boltzmann(MB) distribution. Its translational temperature agrees well with the surface temperature. The fast component exhibits a sharp distribution, and can be fitted to a so-called a shifted maxwellian. The behaviors displayed by the two components are quite complex and depend upon surface temperature, if SR is shone or not, its dose, the history of etching reaction and so on. Examining the data obtained, it is concluded that the effect of excitation by SR on the kinds of desorbed product species and the translational temperature is not in the last process of desorption from surface, but mainly in the process of activation and/or decomposition of a fluorosilyl ($Si_xF_y$) layer formed on the surface. It is found that a fraction of fast component increases when SR is shone on the surface. The details of the results and discussion of a model proposed for synchrotron radiation-excited etching of Si in halogen atmosphere are described in Chapter Ⅲ.

The next materials he tried to etch are carbon containing solids, especially diamond, since it is expected to be chemically inert but is expected to be useful. They have found that SR-excited etching of diamond is successfully done even at low temperatures (as low as -140℃) at which diamond is thermally not oxidized in the gaseous environment. It has been demonstrated

that any of the three types of crystalline diamond, i.e., industrial diamond made at high pressures, thin films grown by chemical vapor deposition, and natural diamond, can be etched by irradiating SR in the $O_2$ atmosphere. From the etched pattern obtained by placing a Ni mesh made of 40 $\mu$ m wires above the sample, it has been found that only the irradiated area is etched and thus surface excitation by SR is essential along with the supply of reactive radical species formed by photodissociation. By selecting the wavelength range of the photons irradiated with and without inserting a carbon filter, the effective wavelength region for diamond etching has been found, that is a photon with an energy over 285 eV, at which an inner shell of carbon can be excited, most effectively contributes to reaction. These results are described in Chapter Ⅳ.

In the last chapter, Chapter V, common features to and different points between SR-excited etching reactions of Si and C-containing chemicals are discussed along with possible future themes in this field.

## 審査結果の要旨

大橋治彦氏は豊橋技術科学大学大学院に５年間在籍し単位取得の上、博士課程を退学し、その後、分子科学研究所で４年半、技官として放射光を利用した研究に従事してきた。

提出された博士論文は、豊橋技術科学大学大学院在学中より現在まで行ってきた放射光励起によるケイ素や炭素を含む固体表面での化学反応についての研究成果をまとめたものであり、審査制度の確立した英文の学術雑誌に掲載された５編の原著論文の内容を含めて構成されている。

論文は三つの主要部分から成る。（１）ケイ素、酸化ケイ素、炭化ケイ素の六フッ化硫黄共存下での放射光励起によるエッチング反応、（２）ダイヤモンド、グラファイトの酸素または六フッ化硫黄共存下での放射光励起によるエッチング反応、（３）ケイ素の二フッ化キセノン共存下での放射光励起によるエッチング反応である。エッチング反応は、共存気体分子の解離、吸着・反応による固体表面層の形成、固体表面からの脱離、の３段階に分けられ、それぞれ異なる波長の光による励起が関わっていると考えられている。大橋氏は各段階で光励起がどのように関わっているのかについて明らかにしようとして以上の３種類の系に対して実験を試み、成功を収めた。

（１）の反応では反応速度の六フッ化硫黄気体の圧力依存性から、フッ素原子の過剰供給条件下では、解離種の吸着・反応によって形成される固体表面層において光励起、特に成分元素の内殻励起が重要であることを見つけた。その応用として（２）のエッチング反応を試み、ダイヤモンドにおいて低温プラズマ法（５０～１００℃）の$10^4$倍もの反応速度を－１４０℃という低温で実現した。励起放射光の波長分布を変化させ反応速度を比較することによって、反応速度が炭素の内殻励起の確率に比例することを明確に示した。さらに（３）ではエッチング反応の結果として放出される中性脱離種それぞれについての運動エネルギー分布を、四重極質量分析管に飛行時間法を組み合わせた独自の装置で測定した。そして光励起のエッチング反応においては、解離種の吸着・反応によって形成される固体表面層が脱離前駆体としての特異的な挙動を示すことを見いだした。

提出された論文の内容を慎重に審査した結果、大橋氏は現象論的な研究になりがちな反応を分子科学的なアプローチを加えて丁寧に研究しており、他に追随を許さない独創的な研究成果を挙げていると判断された。よって、大橋氏の論文は博士論文に値すると審査委員全員が結論した。

また、論文の内容および関連分野についての口述試験を５時間にわたって実施した。研究の動機、研究分野における本研究の位置づけ、実験目的、実験方法、結果、考察などについての説明は明解であり、質疑に対しても的確に答えることができた。関連分野についても十分な基礎知識を有しており、博士の学位を取るのに十分な学力を有していると判断した。論文は日本語で書かれているが、論文要旨と学術誌発表論文から判断して英語力も博士の学位を取るのに十分であると判断した。

また、公開発表会による最終審査にも合格した。