様式Ｃ－１９

# 科学研究費助成事業（科学研究費補助金）研究成果報告書

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研究期間：2009～2010
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研究課題名（和文）超音速分子ビームの立体衝突制御による新規触媒表面の創製
研究課題名（英文）Aligned/oriented molecule-surface interactions: towards the development of new catalysts.
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研究成果の概要（和文）：

本研究では新しい触媒などの開発に向けて、アラインされた分子ビームと表面との反応に関する研究開発がメインの目的です。主な成果は、アルミ、それから水素貯蔵材料として使われている VCrTi の酸化・窒化表面の創製制御・解析である。アライン分子ビームの反応を追及できる研究基盤ができた。詳細結果は投稿論文でまとめている。

研究成果の概要（英文）：
Work during this project has been towards the development of new catalysts etc. making use of reactions between aligned molecules and surfaces. The main results are the study of oxides and nitrides of Aluminium, and hydrogen storage materials such as VCrTi. A base for the study of the interaction of aligned molecules with surfaces has been formed. The detailed results are under consideration for publication.

交付決定額

（金額単位：円）

| | 直接経費 | 間接経費 | 合　計 |
|---|---|---|---|
| 2009 年度 | 2,100,000 | 630,000 | 2,730,000 |
| 2010 年度 | 1,300,000 | 390,000 | 1,690,000 |
| 年度 | | | |
| 年度 | | | |
| 年度 | | | |
| 総　計 | 3,400,000 | 1,020,000 | 4,420,000 |

研究分野：工学
科研費の分科・細目：　応用物理学・工学基礎　薄膜・表面海面物性
キーワード：ビーム応用

## １．研究開始当初の背景

At the beginning of this research project the principal investigator was a member of the group responsible for the surface science endstation at SPring-8's beamline 23SU. This endstation is unique for offering the capability of *in situ* studies of the interaction of a supersonic molecular beam with well defined temperature/kinetic energy with surfaces, using high-resolution synchrotron X-ray photoelectron spectroscopy (XPS) and desorption spectroscopy as the principal diagnostic techniques. Also located at the beamline was a similar 'offline' apparatus, offering similar capabilities but making use of a laboratory X-ray source for XPS studies. Since its development,

the apparatus had been proved to be an excellent tool for characterizing and understanding the oxidization processes of a wide range of clean surfaces, with benchmark results on the oxidation of Si(111), among others. A logical next step on from using a molecular beam with a well-defined kinetic energy is to use an oriented/aligned beam, where the direction of the (or a) molecular axis is defined.

## ２．研究の目的

The aims of the project can be summarized as follows:

(1) Construct and test an aligned molecular beam source, using the velocity selection technique.
(2) Improve the offline apparatus at BL23SU to allow for test experiments using the new source.
(3) Modify the online apparatus to allow for synchrotron XPS studies using the aligned beam source.
(4) Develop analytical techniques related to understanding the interaction of aligned molecules with clean surfaces.

## ３．研究の方法

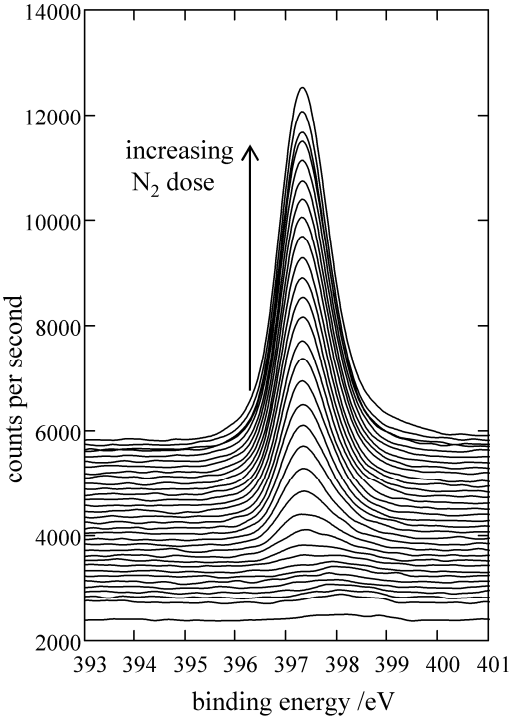
(1) The technology behind molecular beam sources is well-established, and there are many techniques for extending this to making a beam of aligned or oriented molecules. These include the various laser techniques, using single or multiple pulses, cw sources, and ‘field-free` techniques. For polar molecules electromagnetic fields can be used. The approach chosen here was to attempt velocity selection. In a seeded beam (for example $O_2$ expanded in He), each molecule undergoes a large number of collisions with the seed gas. As well as acting to homogenize the kinetic energy distribution, these collisions can have the effect of aligning the molecules, with the degree of alignment depending on the number of collisions. Since the speed of the molecules also depends on the number of collisions, velocity selection can be used to select molecules with high (or low) degrees of alignment.

(2) (related to 4 from above). In order to maximize the information available using synchrotron XPS effort was made to develop analytical techniques for extracting depth profile information from angle-resolved photoelectron spectra. This involves recording the kinetic energy spectra of electrons emitted at different angles to the surface normal. Electrons emitted at larger angles have had to pass through larger numbers of layers, and thus spectra recorded at large angles are more ‘surface sensitive’. In contrast spectra recorded at 0 degrees to the surface normal can be thought of as ‘bulk sensitive’. Electrons emitted from different atoms within the sample have characteristic energies, so recording spectra at several different angles can in principle provide information on the depth distribution of each of the elements present. Combining the technique with photoelectron spectroscopy using synchrotron radiation offers the added advantage that not just individual elements, but also specific sites can be profiled. The approach used in this project was to develop the maximum entropy technique to extract this information, with the ultimate aim of applying this to study the depth profiles of surfaces following interaction with aligned molecular beams.

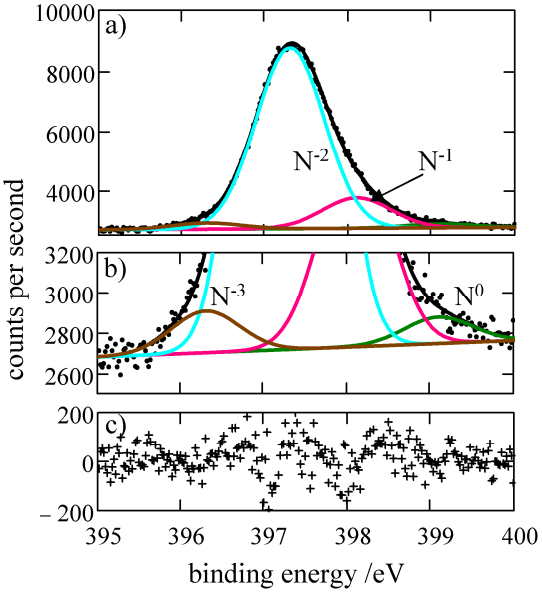
## ４．研究成果

With regard to aims (1) to (3), during the course of this project various aspects of the offline apparatus at beamline 23 were improved in preparation for experiments using aligned beams. The velocity selection technique was investigated theoretically, and parameters determined for a simple velocity selector for selecting aligned $O_2$ molecules seeded in a supersonic helium beam. Concurrently, experiments were carried out online, using synchrotron radiation XPS to study surfaces created using non-aligned beams of $O_2$ and $N_2$, and also using ion implantation. Alongside this work, the technique of depth profiling using angle-resolved XPS data was developed and applied to the data recorded at beamline BL23SU. In more detail: -

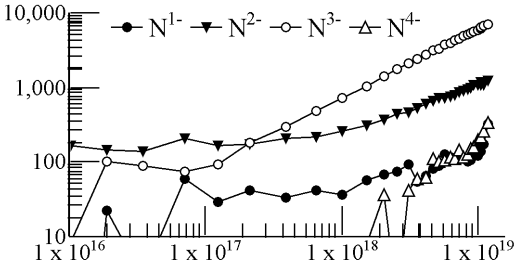
(1) Nitridation of Al. Whereas a clean surface of aluminium readily reacts with oxygen to form $Al_2O_3$, under normal conditions it does not readily react with nitrogen. However AlN is a



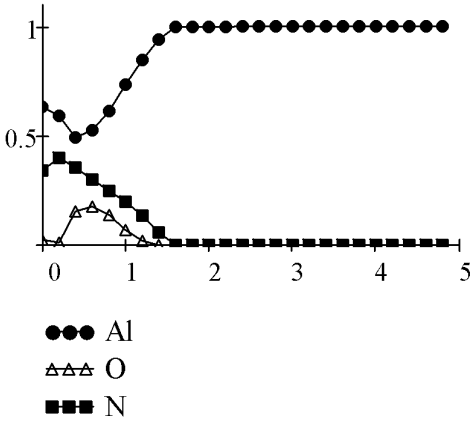

compound with many practical applications (including in photodiodes and heatsinks). As such the investigation of alternative techniques for the production of well-defined AlN thin films is of great interest. The ultimate aim of this investigation is to study the reaction of aligned $N_2$ molecules with clean Al surfaces. As a first step we have successfully studied the reaction




between $N_2$ molecules with kinetic energies of above 2 eV. Using the apparatus at beamline 23 it has been determined that the reaction threshold is around 1.8 eV. Detailed results of this study are currently being



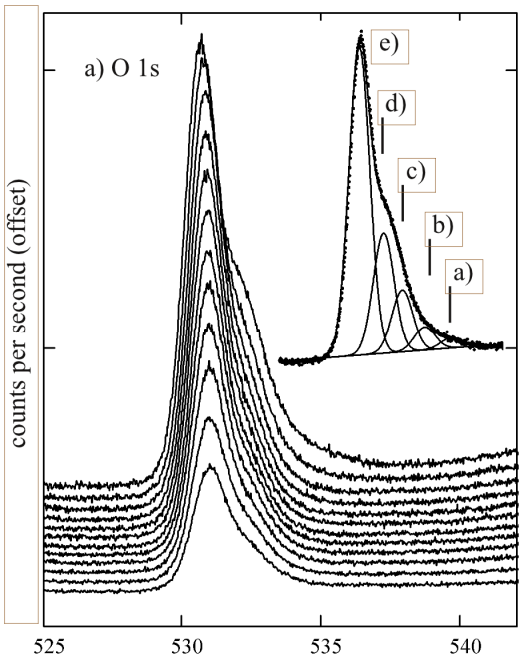

considered for publication. Figure 1 exemplifies the technique behind the study, with N 1s photoelectron spectra recorded during nitridation. The general trend is that the peak height increases with dose. The peak actually consists of four components, as sown in figure 2. By extracting the magnitudes of these components as a function of dose, figure 3 results, which shows that the different components have different uptake curves. The other salient result seen from figure 3 is that no saturation is observed, implying that no protective layer is




formed at these doses. This is in stark contrast to for example the oxidation of Al, where a protective layer prevents further oxidation. Using the depth profiling technique developed as subject (4) of this project, information on the constituents of the thin film was obtained. The results are shown in figure 4, where it is clear that we can see deep penetration of N into the sample. A similar analysis can be performed for each of the 4 components to the N 1s peak - these

results are currently in preparation for publication.

(2) Study of the composition of the natural oxide layer of VCrTi. VCrTi is well-known as a hydrogen storage material, and as such it is of great interest to understand the surface layers, through which hydrogen must pass through during charge and discharge cycles. The ultimate aim here is to create a well-defined surface layer using aligned molecules. As an initial step we have characterized the surface of a natural oxide layer, and also a surface treated by implantation of $D_2$ and D ions. Figure 4 shows O 1s photoelectron spectra recorded at different electron takeoff angles for an untreated VCrTi sample. Using the depth profiling technique developed as subject (4) of this project we have again obtained depth profiles for all 5 of the components of the spectra. Detailed results are currently being prepared as a manuscript for publication, which will also contain related results for samples treated with deuterium ion implantation, to mimic the hydrogen storage process.




５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計１件）

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〔図書〕(計 0 件)
〔産業財産権〕
○出願状況 (計 0 件)
○取得状況 (計 0 件)

〔その他〕
なし

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