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論　文　内　容　の　要　旨

氏　名　（　張　全震　）	
論文題名	Study of Charge States of Oxygen Adatoms on Rutile TiO_2(110) Surface by Atomic Force Microscopy and Kelvin Probe Force Microscopy (原子間力顕微鏡とケルビンプローブ力顕微鏡によるルチルTiO_2(110)表面上の吸着酸素分子の電荷状態と電荷操作に関する研究)

論文内容の要旨

Catalytic reaction based on noble metal nanoclusters on transition metal oxides has fascinated the scientific community for several decades, and it has been widely used in many applications and electronic devices. The prototypical catalytic system of Au nanoclusters on rutile TiO_2 is drawing extraordinary research interest, because of its high catalytic efficiency. In the Au/TiO_2 catalytic system, the physicochemical and electronic properties of the point defects, the adsorbed oxygen adatoms and the Au nanoclusters on rutile TiO_2 can dramatically determine the catalytic activity, which have been investigated by a lot of experimental and theoretical works. However, a large amount of researches about the catalytic reactants have still remained investigation topics, and the catalytic mechanism has not been fully understood yet. It is of high importance to clarify and manipulate the electronic properties of the oxygen adatoms and Au nanoclusters on rutile TiO_2 surface, experimentally and theoretically.

In this doctoral dissertation, I focused on the investigation of charge states of oxygen adatoms on rutile TiO_2(110) surface by noncontact atomic force microscopy and Kelvin probe force microscopy with atomic resolution at 78 K. Firstly, the charge states of the oxygen adatoms were experimentally clarified with atomic resolution for the first time, and the oxygen adatoms were assigned with one and two electrons charged, respectively, depending on the different image contrast. In addition, we measured the values of short-range force and local contact potential difference as a function of tip-sample distance to distinguish the different charge states of the oxygen adatoms. Secondly, we proposed and demonstrated several strategies to manipulate the charge states of oxygen adatoms. For example, the charge states of the oxygen adatoms could be reversibly switched by applying the bias voltage with different polarities and by changing the tip-sample distance, respectively. Thirdly, the conductance states of the oxygen adatoms were investigated depending on its different charge states. We demonstrated that the oxygen adatoms charged by one electron had higher conductance state than that of charged by two electrons, and the conductance behavior of the oxygen adatoms could be reversibly switched between high and low conductance states by manipulating its charge states. In the transition process of the charge state and conductance state of the oxygen adatoms, we proposed that the manipulation mechanism of the reversible switching process was attributed to the tunneling electrons accompanied with the local electric field effects. Fourthly, we demonstrated that the subsurface hydrogen on rutile TiO_2(110) could be characterized by simultaneous multi imaging method with atomic resolution. Four different configurations of the subsurface hydrogen were observed and distinguished with different atomic structures. Moreover, for the first time, the charge distribution of subsurface hydrogen was experimentally clarified to be localized around the nearby subsurface Ti atoms. Besides characterization, we demonstrated that the subsurface hydrogen could be reversibly migrated between the surface and subsurface layers by the voltage pulse with different polarities. Lastly, the charge states of the Au nanoclusters on oxidized rutile TiO_2(110) surface were demonstrated, and the charge transfer between the Au nanoclusters and oxygen adatoms was experimentally clarified. Our present work could contribute to investigation of the catalytic mechanism of the catalytic reactions based on noble metal catalysts on transition metal oxides.

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論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

本学位申請論文（Study of Charge States of Oxygen Adatoms on Rutile TiO_2(110) Surface by Atomic Force Microscopy and Kelvin Probe Force Microscopy）は、表明形状計測手法である周波数変調原子間力顕微鏡（FM-AFM）と表面電位計測手法であるケルビンプローブフォース顕微鏡（KPFM）を組み合わせた複合計測手法を用いて、ルチル型二酸化チタン（TiO_2）単結晶の(110)面に吸着した酸素アドアトムの物性・操作に関する研究をまとめたものである。本論文における主な成果を要約すると以下の通りである。

1．ルチル型TiO_2単結晶の(110)面は、光触媒反応の観点から表面物性・反応に関する研究が盛んに行われている。この表面に酸素分子を吸着させた時の酸素分子や、酸素分子が解離した酸素アドアトムの挙動については、従来、走査型トンネル顕微鏡（STM）を用いて調べられてきたが、STMではこの酸素分子や酸素アドアトムの帯電状態（価数）に関する情報を得ることができなかった。そこで本論文では、FM-AFMおよびKFPMを利用し、表面の酸素アドアトムの高分解能形状・電位観察を行い、その見かけ上の高さや表面電位の違いから、酸素アドアトムの価数（1価ないし2価）を決定することに成功している。

2．探針と酸素アドアトム間にバイアス電圧を印加したり、探針を酸素アドアトムに近づけたりすることで帯電状態（価数）を操作できることを示している。

3．探針から酸素アドアトムへ流れる電流を計測したところ、同じバイアス電圧においてトンネル電流値が異なることを発見し、これを用いて遷移状態を高い時間分解能で計測することに成功し、遷移のメカニズムについて議論している。

4. 表面下の欠陥の可視化に関する研究や酸化した表面上の金（Au）ナノクラスターの物性に関する研究において得られた興味深い結果について述べられている。

以上のように、本研究では、FM-AFM ならびに KPFM を用いてルチル型 TiO_2 単結晶の(110)面に吸着した酸素アドアトムの物性に関して研究したものであり、基礎的な面のみならず、応用の面でも有益な知見が得られており、応用物理学、特に表面物理学の分野に寄与するところが大きい。よって本論文は博士論文として価値あるものと認める。