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主論文の要旨

論文題目　**Controlled Synthesis and Assembly of Two-Dimensional Oxides toward Electronic Applications**
(エレクトロニクス応用を志向した２次元酸化物の精密合成と集積)

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論文内容の要旨

This thesis provides new possibilities to enhance the applicability of two-dimensional (2D) oxide nanosheets. Among various 2D inorganic nanosheets, 2D oxides have attracted wide attention due to their diversity in both structures and functionalities. Despite these potential impacts, applications of the 2D oxides are still very limited compared to the other types of 2D nanosheets (including graphene, h-BN, MoS_2, and so on). The utility of the 2D oxides might be limited by material choice for conducting devices and difficulties in device assemblies. To overcome these issues and expand the utility of the 2D oxides, this thesis focuses on three subjects: (i) controlled doping of 2D oxide nanosheets to explore novel conducting nanosheets (Chapter 2), (ii) development of new device assembly technique (soft optical lithography) for device fabrication (Chapter 3) and studying its application to several types of oxide nanosheets (Chapter 4), and (iii) development of new film assembly technique (Chapter 5) and its application to functional nanocoating (Chapter 6).

Chapter 1 is a background introduction of the doctoral thesis. Chapter 1.1 describes an overall introduction. Chapter 1.2 illustrates a basic introduction about 2D oxide nanosheets, involving preparation and functionalities of 2D oxides. Chapter 1.3 addresses electrical transport characterization and device fabrication techniques of 2D oxide nanosheets. Chapter 1.4 introduces several types of film fabrication methods using 2D nanosheets. With this background information, the motivation and purpose of this thesis is illustrated in Chapter 1.5.

Chapter 2 illustrates exploring novel conducting oxide nanosheets. F doping into both 10-layer $Ti_{0.91}O_2$ nanosheet film and monolayer $Ti_{0.91}O_2$ nanosheet has been successfully conducted by using ultra-low energy ion implantation method. To avoid possible crystal damage, a polymethylmethacrylate (PMMA) layer is used to cover the monolayer $Ti_{0.91}O_2$ nanosheets during ion implantation. By using such ion implantation doping, F ions could substitutionally replace some positions of oxygen without damaging the nanosheet structure. The charge carrier concentration in the F doped $Ti_{1-\square}O_2$ nanosheets can be controlled in the range of 0.3×10^{12} cm^{-2} to 4.0×10^{13} cm^{-2} with increasing implanted ion doses. The monolayer device of F doped $Ti_{1-\square}O_2$ nanosheet with an electron density of $\sim 10^{12}$ cm^{-2} exhibited high electron mobility (over 1,000 cm^2 V^{-1} s^{-1}) even at room temperature, which is of the highest level in oxide semiconductors and inorganic nanosheets.

Chapter 3 describes an easy, fast and cost-effective technique, named LED lithography, for the fabrication of 2D nanosheet device. The LED lithography is a kind of optical lithography that requires only a LED projector, a PC and an optical microscope with a camera and a light source, which suggests the low-cost procedure. In addition, exposure of each designated electrode pattern could be finished within 10s. Two light components of LED projector enables the mask-free patterning: the low-energy red component is applied for the alignment between the electrode pattern and the nanosheets, while the high-energy blue component for exposure photoresists and developing of the alignment marks using PC design patterns. The LED lithography has been utilized for the device assembly of graphene oxide (GO) and $Cs_6W_{11}O_{36}{}^{2-}$ nanosheets. On the other hand, the successful characterizations verify the quality of devices fabricated by LED lithography. Raman spectra of monolayer GO nanosheets and thermal reduced GO nanosheets before and after LED lithography suggest that there is no obvious damage on the GO nanosheets caused by the LED light exposure.

Chapter 4 addresses the application of LED lithography for device fabrication of redox-active RuO_2 nanosheets. As the redox-active RuO_2 nanosheets is rather sensitive to electron beam damage in conventional lithography, it would be a perfect model to confirm the utility of the LED lithography. To study the possible influence of LED lithography on the electrical property of monolayer oxide nanosheets, the current-voltage curve for RuO_2 monolayer film have been monitored before and after LED light exposure by using conductive atomic force microscopy. Finally, the resistivity of individual RuO_2 nanosheets is characterized, which further verify that the optical lithography is a damage-free approach for fabricating nanosheets devices.

Chapter 5 introduces a convenient method, named single droplet assembly, for nanosheet tiling. This method is developed based on the conventional drop-casting technique, while significantly modified the quality of resultant nanosheet films. The nanosheets suspension is simply dropped on the heated substrate to cover the whole surface and then removed by the pipette from the middle bottom of the droplet. Once the suspension is all removed, a nanosheet film could be successfully deposited on the substrate. By introducing ethanol and bottom heating, controlled thermal convection could be generated inside the sessile droplet on a heating plate. Nanosheets inside the sessile droplet would move along such flow and be well organized along the surface of the droplet. Furthermore, the packed nanosheet film would be captured by the droplet surface during the liquid removal procedure.

Chapter 6 illustrates the application of single droplet assembly to various types of nanosheets, substrates and nanostructures. This strategy has been applied to a range of 2D nanosheets, such as $Ti_{0.87}O_2^{0.52-}$, $Ca_2Nb_3O_{10}^{-}$, $Ru_{0.95}O_2^{0.2-}$, and graphene oxide. Neatly tiled ideal monolayer films are successfully fabricated on various types of substrates (including 90nm SiO_2/Si, Pt, $SrTiO_3$:Nb and flexible PET substrate) within ~30 seconds over a wide area (*i.e.*, a 50 mm*f* substrate). The mechanism and control strategies are discussed. We also demonstrate the production of various functional coatings such as conducting, semiconducting, insulating, magnetic, and photochromic coatings in multilayer, superlattice and sub-micrometer-thick forms, offering potential for a convenient way to produce high-quality 2D nanosheet films.

Chapter 7 describes the conclusions of this thesis. First, the main objective of the research is discussed. Second, the significance of the doping engineering for tailored functionality of oxide nanosheets is summarized. Then, the usefulness and importance of the novel device assembly techniques are presented. The prospective for future research related to new functional nanosheets and device assembly are also discussed in this chapter.