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硕士学位论文

$BaTiO_3$片状晶的制备及其在柔性压电发电机中的应用

The Preparation of $BaTiO_3$ Platelets and Its Application on Flexible Piezoelectric Generator

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摘要

本论文采用熔盐法合成了(001)择优取向生长的 $BaTiO_3$ 片状微晶体，利用油/水界面自组装的方法获得了具有高度取向性的压电薄膜，并将其制备成柔性压电发电机用于收集环境机械能。

利用熔盐法在1050℃合成了平板状结构的 $Bi_4Ti_3O_{12}$ 和 $BaBi_4Ti_4O_{15}$ 片状晶体作为前驱体，熔盐介质分别为 NaCl-KCl 和 KCl-$BaCl_2$；然后，在拓扑化学反应阶段 Ba^{2+} 替代 $BaBi_4Ti_4O_{15}$ 中的 Bi^{3+} 形成钙钛矿相的 $BaTiO_3$，反应温度为950℃，熔盐体系为 NaCl-KCl。得到的 $BaTiO_3$ 片状晶体具有较大的径厚比（平均尺寸约为 6~10 μm，厚度为 0.5 μm），并沿(001)择优生长。

利用界面自组装的方法在水/正己烷界面将制得的规则片状晶体装配成了 $BaTiO_3$ 单层薄膜，该薄膜不仅具有较好的致密性，而且片状晶平行于基底表面定向排列。通过理想模型计算了片状晶体在界面以两种不同状态存在时（平行于界面存在、垂直于界面存在）系统界面能的变化量，证明了界面自组装是一个自发进行的过程，驱动力为总界面能的减少。

将组装的 $BaTiO_3$ 压电薄膜转移到溅射一层 ITO 的 PET 基底上，利用 PDMS 封装后制得柔性单层 $BaTiO_3$ 薄膜基压电发电机，为了提高压电发电机的输出性能，利用逐层组装——封装的方法制得了多层 $BaTiO_3$ 薄膜基压电发电机。分别测试了两种压电发电机在 d_{31}（弯曲）、d_{33}（按压）工作模式下的输出性能，并分析了其工作原理。

单层 $BaTiO_3$ 薄膜基压电发电机在按压模式下最大开路电压、短路电流分别为 5.5 V、30 nA，弯曲模式下电压、电流分别为 6.5 V、140 nA；将其用于收集风能，瞬时电压、电流最高可达 2.3 V、96 nA，当外接 80 MΩ 负载时，它的瞬时、平均输出功率分别为 0.055 μW、0.021 μW。

多层 $BaTiO_3$ 薄膜基压电发电机在按压模式下最大开路电压、短路电流分别为 23V、550nA，弯曲模式下电压、电流分别为 24 V、280 nA；将其用于收集波浪能，瞬时电压、电流最高可达 3 V、600 nA，当外接 200 MΩ 负载时，它的瞬时、平均输出功率分别为 1.89 μW、0.383 μW。

制备的 $BaTiO_3$ 薄膜基压电发电机可以驱动数只全屏 LCD 及 LED，证明它具有实用价值。

关键词：$BaTiO_3$ 片状晶、界面自组装、压电发电机

Abstract

In this thesis, micron-scale platelet $BaTiO_3$ with (001) orientation was synthesized using a molten-salt growth method, which was then assembled into film on the oil/water interface by a facile interface self-assembly strategy. Based on the $BaTiO_3$ piezoelectric film, a flexible piezoelectric generator (PG) was developed to harvest the outdoor renewable energy sources such as wind energy and wave energy.

Aurivillius-structured $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$ platelets crystal were first synthesized as precursor by molten-salt growth method in NaCl-KCl and KCl-$BaCl_2$ molten salts, respectively. Then, Bi^{3+} in $BaBi_4Ti_4O_{15}$ was replaced by Ba^{2+} and formed perovskite-structure $BaTiO_3$ through a topochemical reaction at 950℃ in NaCl-KCl molten salt. High aspect ratio $BaTiO_3$ platelets have an average size of 5~10 μm and a thickness of 0.5 μm， which also exhibits a strong (001) orientation.

Well-defined $BaTiO_3$ platelets with rectangle shape were self-assembled at a n-hexane/water interface to fabricate a high coverage area ratio mono-layer nanofilm with a preferred [001] orientation. Using an ideal model in which the $BaTiO_3$ platelets were assumed to be a rectangular platelet, the change in interfacial energy during assembly was calculated exactly, which may be a proof of that it's a spontaneous processes. And the main driving force for the attachment of a $BaTiO_3$ platelet to the oil/water interface during self-assembly is a decrease in total interfacial energy.

The assembled $BaTiO_3$ film was transferred onto ITO coated PET substrate and covered with PDMS to develop flexible PG sbased on monolayer $BaTiO_3$ film and multilayer films with a layer-by-layer method. Subsequently, the output capability of each generator was measured as well as the operating mechanism was analyzed both in d_{31} mode (under vertical stress) and d_{33} mode (under parallel shear force).

When the PG based on monolayer $BaTiO_3$ film working in d_{33} mode, the output open-circuit voltage and short-circuit current reached up to 5.5 V and 30 nA, while in the mode of d_{33} they are 6.5 V and 140 nA, respectively. With the aid of windmill, the

PG produced real-time voltage and current outputs that reached 2.3 V and 96 nA when being employed to harvest the wind energy. The instantaneous outpower and average outpower reached the maximum value of 0.055 μW and 0.021 μW at load resistance of about 80 MΩ, respectively.

In order to improve the output performance, a novel flexible $BaTiO_3$-PDMS multilayer based PG was fabricated. The output voltage and current of the PG device were 23 V and 550 nA, respectively, which was tapped by a ceramic stack. During the bending deformation, the PG device generated maximum electrical signals of 24 V (open-circuit voltage) and 280 nA (short-circuit current). Moreover, a unique equipment was assembled to convert wave energy into electric energy. Being put into a lake, it was lift up and dropped down by the water wave and produced real-time voltage and current outputs which reached up to 3 V and 600 nA. The instantaneous and average outpower reached the maximum value of 1.89 μW and 0.383 μW at load resistance of about 200 MΩ, respectively.

To evaluate the output performance, the PGs were used to harvest ambient energy and successfully drove several LCDs and LEDs. Therefore, the PGs show a promising future for energy generation and self-energy supply.

Keywords: $BaTiO_3$ platelets crystal; interface self-assembly; piezoelectric generator

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