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Emission characteristics of F^- ions into vacuum from CaF_2

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Abstract

Ion emission characteristics from a fluoride ionic conductor were investigated using CaF_2 single crystals. The emission of F^- ions was confirmed by using a quadrupole mass spectrometer, when a positive electric field was applied to the emission surface of the samples under gas pressure around 10^{-3} Pa at 1173 K. Mass spectrometry also revealed that the negative ions emitted from CaF_2 contained a certain amount of O^- ions. It can possibly be explained that the surface of CaF_2 was oxidized in the sample preparation. The emission current from CaF_2 also decreased with the passage of time and increased with applied voltage and temperature. The applied voltage dependence of the emission current did not follow the Schottky equation. In Arrhenius plots, two regions with different slopes were observed, suggesting that there are two ion emission mechanisms with different activation energies.

Keywords: F^- ion; Ionic conductor; Thermionic emission; CaF_2

1. Introduction

In the field of material processing, fluorine ions are used for ion beam implantation [1,2], and reactive ion etching (RIE) [3]. From the practical perspective, the negative fluorine ion (F^-) has a significant advantage as compared with positive fluorine ions. It is known that negative ion beams can suppress the charge-up that causes serious problems such as the dielectric breakdown of the target materials [4,5]. However, because of its difficulty in the production by a conventional discharge plasma method, F^- ion beams have not been widely used yet.

Our group has proposed a novel negative oxygen ion beam (O^-) production method, named solid oxide ion source (SOIS), which utilizes solid oxide ionic conductors [6–9]. The production of O^- ion beam from solid oxide ionic conductor was observed at around 1173 K under vacuum, as has been reported in the earlier works by Torimoto et al. [10–12]. The schematic illustration of the SOIS is shown in Fig. 1. In this system, the production of O^- will be explained as follows: First, oxygen molecules in air adsorb to the air electrode surface, and dissociate into oxygen atoms. Secondly, they change into oxygen anions by capturing electrons, and they are incorporated into bulk of the oxide ionic conductor as oxide ions (O^{2-}). They migrate to the emission surface through the ionic conductor by a gradient of electrochemical potential of oxide ions. On the emission surface, O^{2-} ions change into adsorbed oxygen species, and some of them may still have negative charges. Finally, when an electric field is applied to the emission surface by the extraction electrode that is charged with positive high voltage, these negatively charged oxygen species on the emission surface are emitted into vacuum as negative ion beams.

It is conceivable that the production of F^- ion beams would be possible in a similar way as SOIS by using a fluoride ionic conductor. In this work, the production of F^- ion beams was tested using a CaF_2 single crystal as a fluoride ionic conductor. The characteristics and the mechanism of F^- ion emission will be discussed in detail.

2. Experimental

2.1. Sample preparation

Pellet-type CaF_2 single crystals (Orientation: ⟨100⟩, MTI Corp.) were used for the F^- ion emission experiments in this

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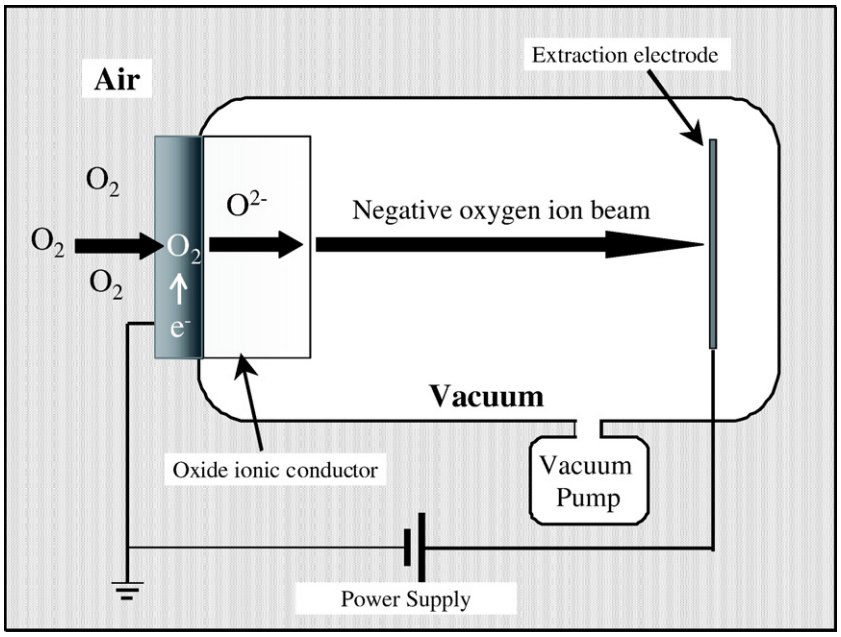

Fig. 1. Schematic illustration of solid oxide ionic source (SOIS).

work. The dimension of emission area was approximately 7.5 mm × 7.5 mm and the thickness of the samples was approximately 0.95 mm. On the opposite surface of the emission surface, Pt paste was sintered at 1173 K for 1 h under dried Ar gas atmosphere. This electrode provides electrons to keep charge neutrality of the sample when negative ions are extracted into vacuum.

2.2. Experimental apparatus

Fig. 2 shows the illustration of the experimental apparatus of the negative ion emission experiment. This experimental apparatus consists of a quartz-glass vacuum chamber, a thermocouple covered with a closed-end alumina tube, a turbo-molecule vacuum pump, a Pt extraction electrode with a 1 mm diameter pinhole, a digital multimeter (ADVANTEST Co., R8240), a DC power supply (Matsusada precision Inc., PL-650-0.1), an external heater, and a quadrupole mass spectrometer (Hiden Analytical Ltd., PSM-003). The vacuum chamber is evacuated to around 10^{-3} Pa by the vacuum pump. The samples were heated by radiant heat of the external heater, and the temperature near the sample was monitored using a thermocouple. A 3 mm gap exists between the pinhole extraction electrode and the emission surface of the sample. When positive voltage was applied to the extraction electrode, an electric

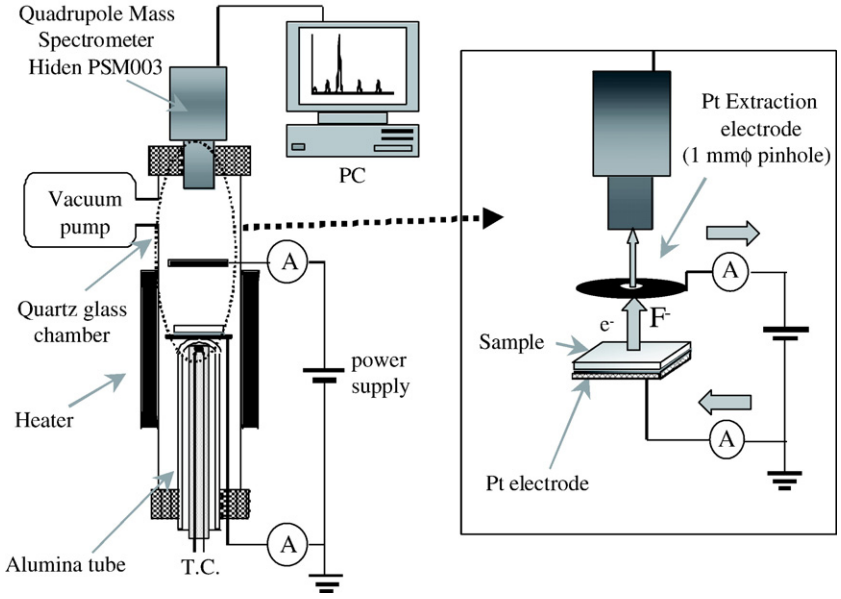

Fig. 2. Illustration of experimental apparatus for negative ion emission from CaF_2.