Microscopic evidence of hydrogen-induced insulation degradation in $BaTiO_3$ revealed by muon spin spectroscopy

T. U. Ito[1,2], W. Higemoto[1,2], T. D. Matsuda[1)*], A. Koda[2,3] and K. Shimomura[2,3]
1) : Research Group for Condensed Matter Physics of Heavy Element Systems, ASRC, JAEA
2): Materials and Life Science Division, J-PARC Center
3): Institute of Materials Structure Science, KEK

In today's electronics industry, multilayer ceramic capacitors (MLCCs) play an important role in the miniaturization of electronic devices, such as smartphones. This is owing to their compactness and high capacitance attributed to a high dielectric constant (κ) of dielectric materials. $BaTiO_3$ is a typical dielectric material used for MLCCs, which exhibits κ~2000 at around room temperature. As in the case of other band insulators, the electronic properties of $BaTiO_3$ can be affected greatly by the introduction of trace amounts of impurities. Therefore, it is important to elucidate the role of impurities in $BaTiO_3$ to control its electronic properties.

Hydrogen is ubiquitous in the environment and can be a native defect in as-grown $BaTiO_3$ crystals. Moreover, fabrication processes of MLCCs (annealing in reducing atmosphere, for example) involve some risks of hydrogen incorporation into the $BaTiO_3$ dielectric layers. We thus focused on the influence of interstitial hydrogen impurities in $BaTiO_3$ on its electrical performance. In general, it is difficult to detect spectroscopic signals directly from such trace amounts of hydrogen impurities. To deal with this difficulty, we used positive muons in place of hydrogen itself. It is well established that a positive muon implanted in matter behaves as a light proton and makes a point defect analogous to interstitial hydrogen impurity [1]. A muon-electron bound state, called muonium, simulates the electronic state of interstitial hydrogen with high accuracy, and muon's radioactive decay enables sensitive detection of the electronic state of the "hydrogen isotope" in $BaTiO_3$.

The muon implantation experiment was performed in the D1 area at the J-PARC muon facility using a high quality single-crystalline wafer of $BaTiO_3$ and an intense positive muon beam. Muon spin rotation and relaxation signals from muons stopped in the $BaTiO_3$ wafer were recorded at cryogenic temperatures down to 2.7 K. The details of the experiment were reported elsewhere [2].

Experimental data showed that a significant fraction of implanted muons bound electrons and formed muonium below ~80 K, as displayed in Fig. 1. The electronic structure of the muonium derived from the hyperfine interaction between the muon and electron spins was quite unusual; the electron cloud spread over several tens of unit cells. Its effective Bohr radius was estimated to be approximately 20 times that in vacuum, suggesting that the electron was very weakly bound to the muon.

The weakly bound electrons were gradually released with increasing temperature due to increased thermal energy as revealed from muonium ionization shown in Fig. 1. The depths of the muonium impurity levels below the conduction band minimum were estimated to be just 4.3(6) and 19(3) meV from the temperature dependence of muonium yield based on an ionization model [1]. These are considerably small in comparison with the band gap: 3.2 eV. The released electrons can move freely around the crystal and cause electric conductivity, thus decreasing the insulating performance of $BaTiO_3$. Interstitial hydrogen impurities in $BaTiO_3$ are also considered to release electrons according to the similar mechanism, resulting in insulation degradation undesirable for capacitor applications.

The insights from this work can be applied to improve the performance of $BaTiO_3$-based MLCCs by reducing the possibility of hydrogen incorporation into the $BaTiO_3$ dielectric layers in their fabrication process.

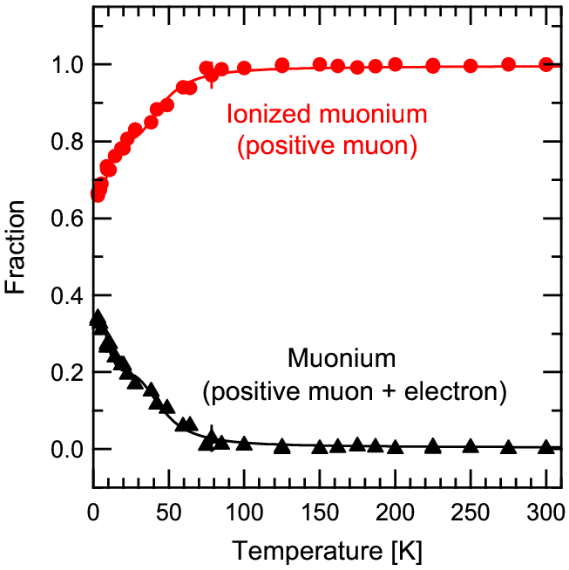

Fig.1 Muonium and ionized muonium fractions as functions of temperature. The solid curves are the best fits to the ionization model [1].

References

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* Present address: Department of Physics, Tokyo Metropolitan University.