Room-temperature Coulomb oscillation of Ni-Nb-Zr-H glassy alloys with nanoscale size clusters†

M. Fukuhara*, H.Yoshida* and A.Inoue**

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1. Introduction

Glassy alloys are peculiar metallic alloys that lack the long-range cyclic order of crystalline alloys, on the nanoscale. Therefore, glassy alloys, which are considered to be macroscopic materials with a mesoscopic system of nanostructures, are candidate materials for future nanoelectronic devices. Following the theoretical pioneering work of Ben-Jacob and Grefen [1] and the subsequent discovery of the Coulomb blockade effect by quantum-dot tunneling at low temperature, [2] a number of studies have reported achievement of room-temperature oscillation. [3]

Recently, Fukuhara *et al*. [4, 5] have observed the electric current-induced voltage oscillation in $((Ni_{0.6}Nb_{0.4})_{0.7}Zr_{0.3})_{1-y}H_y$ glassy alloy ($(0.052 \leq y \leq 0.152)$ at temperature below 240 K, and $((Ni_{0.6}Nb_{0.4})_{1-x}Zr_x)_{1-y}D_y$ ($x=0.30$, 0.35, 0.40 and 0.45, $0.091 \leq y \leq 0.148$) alloys [6] at room temperature. We propose the tunneling of individual protons that are charging and discharging the capacitance of Zr-H(D)-□-H(D)-Zr atomic bond arrays among the Zr(Nb)-tetrahedral sites, where ϒ is the vacancy barrier, termed the free volume, in the glassy alloys. Furthermore, the frequency of the $(Ni_{0.36}Nb_{0.24})_{90.1}Zr_{9.9}$ glassy alloy decreased remarkably with increasing capacitance (C) and resistance (R) in the dc/ac circuit at room temperature.[7] This resembles discharging behavior in which a constant voltage-discharge tube with a parallel condenser and high resistance causes block oscillation, which is derived from the charging and discharging of the capacitance. Thus the glassy alloy could be regarded as a dc/ac converting device with a large number of nanoscopic capacitors.[7] Indeed, the hydrogenated glassy alloy is characterized by an assembly (free volume) of such vacancies (0.7-3 at%), which are distributed homogeneously among the icosahedral clusters. The hydrogen atoms of Ni-Nb-Zr glassy alloys settle stably into four-coordination sites that are surrounded tetrahedrally by four Zr (Nb) atoms, from analysis results of the XAFS spectra using synchrotron radiation photons at SPring-8.[8] Thus we propose the icosahedral Zr-centered $Zr_5Ni_5Nb_3$ cluster (~0.55 nm), as a possible model for the main cluster of the glassy alloy.[9] Since the glassy alloy can be considered a self-organized assembly of low-capacitance, multiple-junction configuration, *i.e*., a huge assembly of 0.5-nm-sized quantum dots, we can expect room-temperature three-terminal transistor.

2. Experimental

The rotating wheel method under an argon atmosphere was used for the preparation from argon arc-melted ingots of amorphous $((Ni_{0.6}Nb_{0.4})_{1-x}Zr_x)_{1-y}H_y$ alloy ribbons of 1-mm width and 20-μm thickness. Hydrogen charging was carried out electrolytically in 0.5 M H_2SO_4 and 1.4 g/L thiourea (H_2NCSNH_2) at room temperature and current densities of 30 A/m^2. [4, 5, 7]

The specific electrical resistances of hydrogenated specimens were measured by the four-probe method. [4-7] The *I-V* curve for the four-probe method was measured from 0 mA to 100 mA with a constant current step of ±0.1 mA at room temperature, using a Semiconductor Characterization System 4200 (Keithley Instruments Inc.). Electrical resistance measurements of onset superconductivity were determined by the temperature dependence of the DC current four-probe method at a cooling rate of 1 K/min from 323 K to 4.2 K in He of ambient pressure under a magnet in the High Field Laboratory (IMR, Tohoku University).

The optional atom configuration and the adiabatic potential energy curve of the icosahedral cluster that consisted of Ni-Nb-Zr-H were calculated by the first-principles density functional calculations using the Vienna *ab initio* simulation package.[8] The nuclei and core electrons are described by the projector augmented plane-wave method and the wave functions are expanded in a plane wave basis set with a cutoff energy of 293.2 eV.

3. Results

The dc electrical resistances of the $(Ni_{0.36}Nb_{0.24}Zr_{0.40})_{90}H_{10}$ glassy alloy were measured in the current region from 1 nA to 100 mA during cooling and heating runs at a temperature region between 300 and 7 K. The maximum amplitude of the Coulomb oscillation

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* IMR, Tohoku University, Sendai, Japan
** Tohoku University, Sendai,, Japan
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increases as the current decreases down to 1μA and then decreases in the lower current region from 100 to 1nA, indicating an occurrence of the optimum current for quantum dot tunnelling between the icosahedral $Zr_5Ni_5Nb_3$ cluster islands.

When we apply a magnetic field to the specimen from 0 to 15 T at 100 and 200 K in parallel and normal directions, we observed the voltage oscillation from around 6 T and 9 T at 100 K and 200 K, respectively. The amplitude of vibration increases with increasing of magnetic field up to 15 T except for a parallel magnetic field above ~12 T at 200 K. Here we should be noted that the chemical potential of the conduction electrons in the ferromagnetic island is affected by magnetic field. This is similar to variation in electrostatic potential caused by gate voltage in field electrostatic transistor (FET). By analogy, we infer that application of magnetic field induces Coulomb oscillation derived from noticeable variation in the chemical potential of an isolated ferromagnet (island) in ferromagnetic fields. In this study, the ferromagnetic metal responsible for the magneto- Coulomb oscillation is Ni alone, because Zr and Nb are nonmagnetic elements. In the atomic configuration of $Ni_5Zr_5Nb_3$ cluster, five Ni atoms are separately coordinated against Zr and Nb atoms.[8]

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