A proton dot tunneling in a Ni-Nb-Zr-H glassy alloy with multiple junctions

Mikio Fukuhara, Shinichi Yamaura and Akihisa Inoue

Institute for Materials Research, Tohoku University, Sendai, Japan 980-8577

E-mail: fukuhara@imr.tohoku.ac.jp

Abstract. Following the discovery of Coulomb oscillation by the proton tunneling in Ni-Nb-Zr-H glassy alloys, we investigated the temperature-dependent hydrogen effect for dc electric conduction of the (Ni_{100-x}Nb_{24}Zr_{40})H_{x} (0≤x≤15.7) glassy alloys. Electric current-induced voltage oscillation at 660 kHz and evidence of the Coulomb staircase of I-V characteristics show Coulomb oscillation in nanoscopic size tunnel junctions arranged in a low-capacitance, based on proton resonance among the multiple-junctions of the glassy alloys in the temperature range of 240 K to 6 K.

1. Introduction

Coulomb dot tunnelling is current topics in physics. Many research groups have studied the ‘Coulomb blockade’ effect, in which charge transport through the device occurs in an electron-by-electron manner at low temperatures [1-4]. The Coulomb blockade effects of single electron and photon in mesoscopic systems with nanostructures show nonlinear responses to the externally connected macroscopic system.

In a previous papers [5,6], an electric current-induced voltage oscillation at 500-740 kHz was observed in the current-voltage curves of nanoscopic size (~0.9-nm) tunnel junctions arranged in a low-capacitance (~1aF), multiple-junction configuration of (Ni_{42}Nb_{28}Zr_{30})H_{x} (5.2≤x≤15.2) and (Ni_{36}Nb_{24})_{100-y}Zr_{y}D_{z} (9.1≤z≤14.8)glassy alloys, which consist of antinomic affinity Zr and antiaffinity Ni elements for hydrogen, in the temperature range of 373 K to 6 K. The discreteness of the proton and deuteron charge could cause dramatic transport phenomena in glassy alloys with nanostructures. In sharp contrast to crystalline materials with high hydrogen content, by cooperative motions of hydrogen, furthermore, hydrogen atoms in the Ni_{42}Nb_{28}Zr_{30} glassy alloy strongly settle into four-coordination sites surrounded tetrahedrally by four Zr atoms [7].

In order to enhance the transition temperature, the temperature-dependent hydrogen effect for electric conduction of the (Ni_{100-x}Nb_{24}Zr_{40})H_{x} (0≤x≤15.7) glassy alloys was investigated in anticipates of strong affinity of zirconium to hydrogen. Glassy alloys are peculiar metallic alloys in that they lack the short-, medium-or long-range cyclic order of crystalline alloys, on the nanoscale [8-10]. Therefore, the glassy alloy is considered to be a macroscopic material with a mesoscopic system that consists of nanostructures.

2. Experimental

The rotating wheel method under an argon atmosphere was used for the preparation of glassy Ni_{36}Nb_{24}Zr_{40} alloy ribbons of about 1mm width and 20 μm thickness from argon arc-melted ingots. Hydrogen charging was carried out electrolytically in 0.5 M H_{2}SO_{4} and 1.4g/L thiourea (H_{2}NCSNH_{2}) at room temperature and at the current densities of 30 A/m². The amounts of hydrogen absorbed in the specimens were measured by the inert gas carrier melting-thermal conductivity method. The structure of the (Ni_{36}Nb_{24}Zr_{40})H_{x} glassy alloys was identified by X-ray diffraction with Cu Kα radiation at grazing incident mode.

The specific electrical resistance of hydrogenated specimens was measured by the four-probe method dc and ac source 6221, Nano Voltmeter 2182A; with a dc current of ±1 mA at cooling and heating rates of 1 K/s from 323 K to 6 K in He of ambient pressure. The distance between the two
voltage electrodes was 20 mm. In order to eliminate both the effects of the electromagnetic environment and the quantum fluctuation of electric charge [11], we used a source resistance (Rs) of 10 GΩ, which is much larger than the quantum unit of resistance $R_Q = h/e^2$. The four-probe method I-V curve was measured from -1.0 to + 1.0 mV and then from + 1.0 to -1.0 mV by constant voltage step of 0.05mV at temperature region from 400 to 7 K, using Semiconductor Characterization System 4200 with an accuracy of ±5μV. Voltage oscillation was measured by an oscilloscope and the power spectrum was analyzed by FFT.

3. Results and discussions

3.1. Temperature dependence of electric resistivity

The electrical resistances of (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{100-x}$H$_x$ (x=0～15.7) alloys under 1 mA dc current with positive sign were measured during cooling and heating runs. The results are shown as a function of temperature (Figure 1). The resistance of the Ni$_{36}$Nb$_{24}$Zr$_{40}$ alloy without H increased almost linearly with decreasing temperature. The negative temperature coefficient of resistivity (TCR) of -1.209x10^{-5}/K indicates a semiconducting character. The resistivity of the (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{89.3}$H$_{10.7}$ alloy initially showed the similar negative TCR behaviour as the alloy without H, but suddenly increased to 2nd to 3rd order (Figure 2) at 113 K, and then continued with discrete variation down to 8 K. Subsequently, the resistance dropped abruptly on the extended line of the cooling curve between 323 K and 113 K, and then ascended once again as the temperature decreased. In the heating run, the resistivity decreased according to the same curve as the cooling run, except for an increase between 10 and 220 K (Figure 2). We observed the similar abnormal resistivity variations for (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{90.6}$H$_{9.4}$, (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{90.7}$H$_{9.3}$, (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{87.4}$H$_{12.6}$ and (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{89.7}$H$_{10.3}$, but not for (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{97.8}$H$_{2.2}$, (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{95.5}$H$_{4.5}$, (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{78.5}$H$_{21.5}$ and (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{72.2}$H$_{27.8}$. Consequently, the abnormal variations in the two runs occurred at restricted hydrogen concentrations of 9.4 to 12.3 at% H. The negative TCR increased linearly as the hydrogen content increased (insert, Figure 1).

3.2. DC current-induced AC oscillation

The abrupt increases noted in the two runs mirror the metal-to-insulator transitions (Mott transitions) of vanadium and titanium oxides at the Neel temperature [12]. However, since the voltage showed negative sign and the voltage variation did not follow the Ohmic rule in the restricted temperature range, we observed the variation. The power spectrum of the representative

Figure 1. Electric resistivity of (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{100-x}$H$_x$ (x=0～15.7) alloys. Insert: Effect of hydrogen on TCR

Figure 2. Abnormal resistivity of (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{100-x}$H$_x$ (x=0～15.7) alloys.

Figure 3. Power spectrum.
(Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{89.3}$H$_{10.7}$ alloy is shown in Fig.3, indicating an ac saw wave with voltage oscillation of 660 kHz. This value is somewhat larger than the tunneling frequency (543 kHz) of proton in previous paper [5]. The frequency depends on capacitance of the circuit, described later. The detailed results will describe in the following paper. Thus it is clear that this abnormal behaviour is a dc current-induced ac oscillation, which is associated with the quantum mechanism of solute hydrogen. This oscillation is suggested to arise from sequential quantised charging of the sample.

3.3. Temperature dependence of $I$-$V$ characteristics

To certificate the current mechanism reasonably, we then measured $I$-$V$ characteristics at temperatures ranging from 6 to 400 K, because a stepwise increase of the current $I$ upon increasing the bias voltage $V$ is expected for tunnel barriers [13]. Figure 4 is typical Coulomb staircase, showing typical quantum dot tunneling. The width $\Delta V = 0.17$ mV of the current plateaus is a direct measure of the charging energy: $e \Delta V = e^2/C$, from which we deduce the total capacitance $C = 0.9$ fF at 300K. To evaluate the tunnel barrier height, the current is plotted as a function of the inverse temperature ($1/T$), the Arrhenius plot in Fig.5, measured for the fixed $V = 0.13$ mV. It can be seen that there are two distinct temperature regions. At temperature below ~240K, the current is almost constant, whereas it increases fairly with increasing temperature. The former behaviour is based on the tunneling [14], and the latter one is an activation process that arises from the thermionic emission over the tunnel barrier [15]. From the slope in the higher temperature region, the activation is estimated to be ~ 245 meV. The value is larger than that (173 meV) of nanocrystalline silicon single-electron transistors [16]. Based on the present results, it is possible that the abnormal behavior of interest is a Coulomb oscillation that arises from the tunnelling of an individual proton charging and discharging the capacitance, thereby producing discrete voltage jumps with $3^{rd}$ order of $e/C$ in Ni-Nb-Zr-H glassy alloys.

In previous papers [5,6], we proposed a schematic representation of a microscopic junction between two Zr-tetrahedral clusters, surrounded by four Zr and Nb atoms, belonging to each icosahedron-like polyhedron in the Ni-Nb-Zr-H glassy alloy, because the glassy alloys can be viewed as an assembly of the zigzag icosahedron-like polyhedron [17]; An atomic Zr-H-□-H-Zr array [~0.9 nm (Ref.18)] corresponds to a single Coulomb blockade tunneling junction, where □ is a vacancy barrier with electrostatic capacitance $C$ between tetrahedral clusters. The glassy alloy is characterized by an assembly (free volume) of such vacancies, which are distributed homogeneously among the clusters. Thus the tunneling junction representing a single element of the array is characterized by a tunneling resistance $R_t$ and capacitance $C$ in the equipment circuit (Fig.4b in Ref.5).

Cessation of oscillation may be explained by the phase transition of the electrical circuit. Morimoto [20] has reported that an oscillatory-nonoscillatory transition of discontinuous waves is induced in a blocking oscillation by connecting a variable resistor $R$ in parallel to the capacitor that decides the

![Figure 4. $I$-$V$ characteristics of (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{89.3}$H$_{10.7}$ alloy.](image)

![Figure 5. Arrhenius plot of the current for (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{89.3}$H$_{10.7}$ alloy.](image)
frequency of the circuit. Therefore, we infer by analogy that the oscillation ceases when $R$ decreases relative to the circuit resistance $R_c$ due to a decrease in tunneling resistance at low temperature. This interesting study provides new insight into the transport mechanism.

4. Conclusions
Characteristic electric resistivity of the (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{100-x}$H$_x$ ($0 \leq x \leq 15.7$) glassy alloys was measured in the temperature region between 323 and 6K. The resistivity showed abnormal variations at restricted proton concentrations of 9.4-12.3 at%. The power spectra for wave patterns of the representative the (Ni$_{36}$Nb$_{24}$Zr$_{40}$)$_{89.3}$H$_{10.7}$ alloy showed voltage oscillation of 660 kHz, being somewhat larger than that (543 kHz) of proton tunnelling. The I-V characteristics at temperatures ranging from 6 to 400 K revealed the Coulomb staircase, indicating typical quantum dot tunneling in the atomic Zr-H-C-H-Zr array. Assuming from the hydrogen atom environment are tetrahedrally surrounded by four Zr and Nb atoms, we proposed the schematic representation of the microscopic junction between two Zr-tetrahedral clusters belonging to each icosahedron-like polyhedron in the Ni-Nb-Zr-H glassy alloy. Thus, it is clear that this abnormal behaviour is the dc current-induced ac oscillation, which is associated with the quantum mechanism of solute proton. In a subsequent paper, higher temperature tunnelling will be described: attention will be given to the proton dot resonance occurring at room temperature.

Acknowledgement. This work was supported by a Grant-In-Aid for Science Research in a priority Area ’Research and Development Project on Advanced Metallic Glasses, Inorganic Materials and Joining Technology’ from the Ministry of Education, Science, Sports and Culture, Japan, and by JSPS Asian CORE Program.

References
[1] Ben-Jacob and Grefen Y 1985 Phys.Lett. 108A 289.
[2] Kastner M.A, Kwasnick P.F and Licini J.C 1987 Phys.Rev. B. 36 8015.
[3] Fulton T.A and Dolan G.J 1987 Phys.Rev.Lett. 59 109.
[4] Ono K, Shimada H and Ootuka Y 1998 J.Phys.Soc.Jpn. 67 2852.
[5] Fukuhara M, Kawashima A Yamaura S and Inoue A 2007 Phys.Stat.Sol.(RRL) 1 R50.
[6] Fukuhara M and Inoue A 2008 Europhys.Lett. 83 36002.
[7] Fukuhara M, Kawashima A, Yamaura S and Inoue A 2007 Appl.Phys.Lett., 90 203111.
[8] Edier M.D 2000 Ann.Rev.Phys.Chem. 51 99.
[9] Fan G.J and Fecht H.J 2002 J.Chem.Phys. 116 5002.
[10] Yavari A.R. 2006 Nature, 439 405.
[11] Furusaki A and Ueda M 1992 Phys.Rev.B, 45 3435.
[12] Adler D, Feinleib J, Brooks H and Paul W 1967 Phys. Rev. 155 851.
[13] Likharev K.K 1989 IBM.J.Res.Dev. 32 144.
[14] Tsuya D, Suzuki M, Aoyagi Y and Ishibashi K 2005 Microelectro.Eng 82 196.
[15] Martel R, Derycke V, Lavoie C, Appenzeller J, Chan K.K, Tersoff J.and Avouris Ph. 2001 Phys.Rev.Lett. 87 256805.
[16] Tan Y.T, Kamiya T, Durrani Z.A.K and Ahmed H 2003 J.Appl.Phys. 94 633.
[17] Takeuchi A,Yabuta K,Yokoyama Y, Makino A and Inoue A 2008 Intermetallic, 16 283.
[18] Westlake D,G, Shaked H, Mason P.R, McCart B.R., Mueller M.H, Matsumoto T. and Amano M 1982 J.Less-Common Metals 88 17.
[19] Takagi T, Ohkubo T, Hirotsu Y, Murty B.S, Hono K, and Shindo D 2001 Appl.Phys.Lett. 79 485.
[20] Morimoto Y 1983 J.Phys.Soc.Jpn. 52 1086.