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ac impedance analysis of a Ni-Nb-Zr-H glassy alloy with femtofarad capacitance tunnels

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A Nyquist diagram of a (Ni0.36Nb0.24Zr0.30)0.06H10 glassy alloy shows a semitrue circle, indicating that it is a conducting material with a total capacitance of 17.8 μF. The Bode plots showing the dependencies of its real and imaginary impedances, and phase on frequency suggest a simpler equivalent circuit having a resistor in parallel with a capacitor. Dividing the total capacitance (17.8 μF) by the capacitance of a single tunnel (0.9 fF), we deduced that this material has a high number of dielectric tunnels, which can be regarded as regular prisms separated from the electric-conducting distorted icosahedral ZrNi3Nb3 clusters by an average of 0.225 nm. © 2010 American Institute of Physics. [doi:10.1063/1.3294294]

Following the theoretical pioneering work of Ben-Jacob and Grefen1 and the subsequent discovery of the Coulomb blockade effect by quantum-dot tunneling at low temperature,2,9 a number of studies have reported the achievement of room-temperature oscillation.4–9 Recently, Fukuhara et al.10,11 have observed the electric current-induced voltage oscillation in [(Ni0.6Nb0.4)1−yZry]Hy glassy alloys (with 0.052<y<0.152) at temperatures below 240 K, and [(Ni0.6Nb0.4)1−yZry]Dy alloys (with x=0.30, 0.35, 0.40, and 0.45, and 0.091<y<0.148)12 at room temperature. Following these two-terminal Coulomb dot oscillations, we realized the room-temperature switching, Coulomb blockade, and memory effects in a millimeter-sized three-terminal glassy alloy field-effect transistor.13 Thus, we regarded it as a dc/ac converting device with a large number of nanometer size capacitors. However, conducting alloys, which can store charges, have not been observed, except for offspring structures, which were born charged under high pressure.14

Here, we note that glassy alloys are characterized by an assembly of vacancies which occupy between 0.7% and 3% of the total volume.15 The number of such vacancies increases as the doping with hydrogen increases. To investigate the distribution state of vacancies in eccentric glassy alloys, we determined the ac impedance of a glassy alloy consisting of nanometer-sized clusters.16 In this letter, therefore, we attempted to examine the physics of such a system in the case where the impedance of the nanometer-size clusters became an important consideration. Significantly, no research work has been carried out previously on the ac impedance analysis of Ni-Nb-Zr-H glassy alloys with femtofarad capacitances. Our results indicate that such glassy alloys have potential applications as nonwired, room-temperature quantum devices such as batteries, amplifiers, and memory switches.

The rotating wheel method applied in an argon atmosphere was used for the preparation of glassy alloy Ni0.36Nb0.24Zr0.30 ribbons with a width of about 1 mm and a thickness of about 40 μm made from argon arc-melted ingots. Hydrogen charging was carried out electrolytically in 0.5 M H2SO4 and 1.4 g/L thiourea (H2NCSNH2) at room temperature and at a current density of 30 A/m2, using a Pt counter electrode.10,11 The structure of the (Ni0.36Nb0.24Zr0.30)0.06H10 glassy alloy (with a density of 6.80 Mg/m3 and porosity of 2.57%) was identified by x-ray diffraction with Cu Kα radiation in the grazing incident mode.

The four-terminal pair configuration on LCR Meter E4980A measured the complex impedance at frequencies between 20 Hz and 2 MHz under a constant voltage of 20 mV at room temperature, to remove undesirable influences such as noise derived from electromagnetism in the environment, interference of the test signals, or unwanted residual factors in the connection method incidental to ordinary termination methods. The distance between the two electrodes was 10 mm. Two gold wires each having a diameter of 100 μm were welded to the glassy alloy, to avoid the interfacial impedance effect of the semiconducting oxygen-rich layer. The signal path connection between the specimen and the LCR Meter was made as short as possible. Before each run, we touched the round wire to completely eliminate any offset charge. All electronic measurements were carried out in an Al shield box, to prevent electromagnetism of the environment from influencing the results. The real and imaginary parts of the complex impedance were calculated by the software program VEE (Agilent Technologies). Finally, we compared the data on the glassy alloy with the experimental data on integrated ceramic condenser composed of 1 μF (Mu-
rata), 0.47, and 0.22 μF (NEC-Tokin), to certify our results.

To nondestructively analyze electronic contribution of the glassy alloy without grain boundaries, we measured the ac impedance in a simple circuit in which the specimen was integrated at room temperature, as a function of the applied frequency. The Nyquist (complex impedance plane) plot for the (Ni$_{0.36}$Nb$_{0.24}$Zr$_{0.40}$)$_9$H$_{10}$ alloy is shown in Fig. 1, along with that of a ceramic condenser. For the measurement of the ceramic condenser, we used an equipment circuit composed of the same capacitance and resistance as the glassy alloy. The alloy’s variation in impedance with frequency followed a semicircle, showing an ideal Debye relaxation peak, which usually cannot be obtained in ordinary electrochemical and dielectric measurements. This phenomenon could be derived from the alloy’s nanometer size configuration, which lacks dispersion factors such as interface, grain boundary and inclusion. A reactance, $R_C$, of 6.6 Ω and a relaxation time, $RC_{\text{total}}$, of 1.2 × 10$^{-4}$ s at the summit of the semicircle were derived from the formula $RC_{\text{total}} = 1/(2\pi f_{\text{max}})$, where $f_{\text{max}}$ (=1350 Hz) is the frequency of the peak. Thus, the total capacitance, $C_{\text{total}}$, of the specimen was calculated to be 1.8 × 10$^{-5}$ F. Similarly, the Nyquist diagram of the ceramic condenser in Fig. 1(b) also shows a similar semicircle. The total capacitance of the ceramic condenser can, thus, be calculated as 1.6 × 10$^{-5}$ F, from $R = 8.3$ Ω, $RC_{\text{total}} = 1.3 × 10^{-4}$ s, and $f_{\text{max}} = 1200$ Hz.

The Bode plots shown in Fig. 2 illustrate the dependencies of the impedance ($Z$) and phase ($\theta$) on the frequency ($f$) for the (Ni$_{0.36}$Nb$_{0.24}$Zr$_{0.40}$)$_9$H$_{10}$ alloy (a) and ceramic condenser (b) at room temperature.

FIG. 2. (Color) Bode plots showing the impedance ($\log Z$) and the phase ($\theta$) vs the frequency ($\log f$) for the (Ni$_{0.36}$Nb$_{0.24}$Zr$_{0.40}$)$_9$H$_{10}$ glassy alloy (a) and the ceramic condenser (b) at room temperature.

FIG. 3. (Color) Bode plots showing the real impedance ($\log Z'$) and the imaginary impedance ($\log Z''$) vs the frequency ($\log f$) for the (Ni$_{0.36}$Nb$_{0.24}$Zr$_{0.40}$)$_9$H$_{10}$ glassy alloy (a) and ceramic condenser (b), as well as the relation (c) between $\log Z'/\log Z''$ and $\log f$ for the glassy alloy and ceramic condenser at room temperature.

FIG. 4. (Color) (a) Configuration pattern of insulating zigzag tunnels among the distorted icosahedral Zr$_5$Ni$_5$Nb$_3$ clusters (quantum dots) arranged at intervals of 0.225 nm (b) A glassy alloy has numerous insulating nanotunnels among conducting clusters.

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continued to rise up to 2 MHz. These results also suggest the parallel circuit of \( R \) and \( C \) [Fig. 1(b), inset]\(^9\) for the ceramic condenser.

Graphs of real impedance (log \( Z' \)) and imaginary impedance (log \( Z'' \)) against the frequency (log \( f \)) in another Bode plot are presented at Figs. 3(a) and 3(b) for the alloy and the ceramic condenser, respectively. The real impedance of the glassy alloy remained constant up to 600 Hz and then substantially decreased as a sixth-order polynomial. The imaginary impedance curve shows one peak with a maximum value at \( f_{\text{max}}=2000 \) Hz. The slopes of the linear lines of the imaginary impedance curve are +0.85 and −0.96 for ideal values +1 and −1, respectively. Similarly, the real and imaginary impedances curves of the ceramic condenser resemble those of the glassy alloy. The slopes of the imaginary impedance curve of the ceramic condenser are +0.81 and −0.86. The glassy alloy shows ideal impedance characteristics between frequencies of 20 Hz and 2 MHz. The ratios of log \( Z'/Z'' \) for both materials are shown in Fig. 3(c). They reveal the same tendency at a glance. This is a type of dielectric function. The logarithmic singularity appears at around 3.5 and 4.5 kHz for the glassy alloy and ceramic condenser, respectively. Thus, these experimental results distinctly indicate the existence of capacitance in the glassy alloy and provide evidence of marked frequency-induced conductivity.

From these results, we hypothesize the existence of numerous dielectric tunnels in the glassy alloy. Dividing the total capacitance (17.8 \( \mu \)F) by the capacitance of a single tunnel (0.9 \( \mu \)F),\(^{11} \) the number of tunnels was calculated to be \( 2.0 \times 10^{10} \). Because the volume of the specimen was 0.60 mm\(^3\) (0.04 \( \times \) 1.0 \( \times \) 15 mm\(^3\)), the free volume of 2.57% was 0.015 mm\(^3\). Assuming that the tunnel is a regular prism of side \( d \) and a length of 15 mm, we obtain the side
\[
d = \sqrt[3]{0.015/2.0 \times 10^{-15}} = 0.225 \text{ nm.}
\]

Based on the analysis of the X-ray absorption of fine structure spectra using strong radiation photos taken at the SPring-\( \text{\textregistered} \) and the \textit{ab initio} calculation,\(^{20} \) we propose a configuration pattern oficosahedral \( \text{Zr}_5\text{Ni}_3\text{Nb}_5 \) clusters (≈1 nm) combined with small amounts of other Voronoi-type polyhedra separated by insulating zigzag tunnels of size 0.225 nm [Fig. 4(a)]; the Voronoi-type polyhedral portion is not shown]. The results indicate that the glassy alloy can be considered a self-organized assembly of femtofarad-capacitance, multiple-junction configurations; in other words, a huge assembly of 1-nm-sized quantum dots produced by hydrogen doping in addition to rapid quenching. This means that electric charge can be stored in nanotunnels [Fig. 4(b)] of conducting glassy alloys, leading to cluster electronics without wiring.

In conclusion, ac impedances of the \((\text{Ni}_{0.36}\text{Nb}_{0.22}\text{Zr}_{0.40})_8\text{H}_{10}\) glassy alloy were measured at frequencies between 20 Hz and 2 MHz at room temperature and compared with the impedances of a ceramic condenser in the same frequency range. The Nyquist diagram for both materials showed the semicircle, suggesting a simple equivalent circuit composed of a parallel combination of \( R \) and \( C \). The slopes of log \( Z' \) and log \( Z'' \) against log \( f \) in the glassy alloy revealed ideal dielectric characters throughout the entire measured frequency region. Dividing the total capacitance by the capacitance of a single tunnel, we calculated that the alloy has a high number (2.0 \( \times \) 10\(^{10} \)) of insulating zigzag tunnels of an average size 0.225 nm among the electric-conducting distorted icosahedral \( \text{Zr}_5\text{Ni}_3\text{Nb}_5 \) clusters. This finding will facilitate the development of nanometer size electronics based on cluster science.

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