Pressure Dependence of Hopping Conduction in Amorphous Ge alloys

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Abstract. The ac-conductivity of amorphous Ge-Au alloy has been measured at frequencies of 20 Hz to 1 MHz, at pressures up to 5 GPa and temperatures down to 77 K using a Drickamer-type high pressure cell. The ac-conductivity increases with increasing frequency. With increasing temperature, the rising frequency increases. From these results, temperature dependence of conductivity was obtained without shape parameters of the sample. The temperature dependence of hopping conductivity is found to be well described by a power law expected from the Multiphonon Process model. The exponent $n$ in the power law increases with increasing pressure below 2 GPa, and decreases above 2 GPa. This pressure dependence of $n$ agrees with the previous reported results from dc electrical resistivity measurements. The anomalous pressure dependence of $n$ is discussed in relation to the Debye frequency, atomic distance, void size, and the density of states at the Fermi level.

1. Introduction
Amorphous semiconductors have localized states in the energy gap. At low temperature, the electrical transport occurs by hopping of these localized electrons. For the mechanism of hopping conduction, a variable-range hopping (VRH) model was suggested by Mott, and it is well known as the $T^{-1/4}$ law [1]. However, there are some problems in VRH: for example, the value of density of states at the Fermi level calculated by the formula of $\sigma$ is far from the expected value. One of the reasons is that VRH assumes homogeneously distributed localized states. So Shimakawa proposed multiphonon hopping process (MPP) of deep localized electrons between microvoids, which assumes inhomogeneous distribution of localized states [2]. In MPP, $\sigma$ is proportional to $T^n$ and the frequency dependence of the ac conductivity is given by

$$\sigma(\omega) = \sigma_0 \left[ i \omega \tau / \ln(1+i\omega\tau) \right].$$

It is difficult to find which mechanism dominates because the temperature dependence of electrical conductivity for each theory seems to explain the measurements in the limited temperature range. High pressure studies on the electrical transport properties are expected to be effective, because different pressure dependence of the parameters in each model gives different pressure dependence of $\sigma$. And so in order to clarify which model is appropriate, the pressure dependence of electrical resistivity was studied in our group so far [3-5]. However, it was difficult to estimate $\sigma$ from the
resistivity measurement for brittle amorphous material because sample may change its shape by applying pressure.

In this paper, the frequency dependence of ac conductivity under pressure was measured. The value of $\sigma$ can be estimated from the frequency dependence alone, no matter how the shape of the sample changes.

2. Experimental
The ac conductivity of amorphous (a-) Ge$_{0.99}$Au$_{0.01}$, whose resistivity is smaller than that of a-Ge, was measured up to 5 GPa and at temperatures of 77-300 K. Pressure was generated by a Drickamer-type high pressure cell. It consists of the opposed tapered anvils of tungsten carbide, the cylinder of beryllium-copper alloy, pyrophyllite pellets, and electrodes. Each anvil has a center face of 2 mm in diameter. The absolute value of admittance and phase angle was measured by an LCR meter from 20 Hz to 1 MHz. For low temperature measurements, the cell was cooled by liquid nitrogen down to 77 K. Temperature was measured by copper-constantan thermocouples. Details of the experiment were described elsewhere [3-5].

3. Results
Figure 1 shows the frequency dependence of ac conductivity for a-Ge$_{0.99}$Au$_{0.01}$ at various temperatures at 3.0 GPa. As the frequency increases, the ac conductivity eventually starts to rise at each temperature. This is a behavior characteristic of disorder systems in contrast with Drude’s model, where ac conductivity decreases with increasing frequency. The frequency at which the ac conductivity starts to rise is given $\tau^{-1}$ in eq.(1). From figure 1, we can see that $\tau^{-1}$ increases with increasing temperature. The temperature dependence of $\tau^{-1}$ at various pressures are shown in figure 2. As $\tau^{-1}$ has the same meaning as the hopping conductivity, figure 2 shows the temperature dependence of hopping conductivity. Temperature dependence of hopping conductivity obeys the power law as expected from the MPP model. The exponent $n$ in the power law varies with increasing pressure as shown in figure 3. It is found that the value of $n$ increases below 2 GPa, and decreases above 2 GPa. The results of the pressure dependence of $n$ from the previous reported dc electrical resistivity experiments for a-Ge, a-Ge-Al, and a-Ge-Cu alloys are also shown in figure 3 for reference. From both ac conductivity measurements and dc electrical resistivity measurements, it is found that with increasing pressure $n$ increases in low pressure region and decreases in high pressure region.

![Figure 1](image1.png)
**Figure 1.** The ac conductivity of an amorphous Ge$_{0.99}$Au$_{0.01}$ as a function of frequency at various temperatures at 3.0 GPa.

![Figure 2](image2.png)
**Figure 2.** Log-Log plot of hopping rate of a-Ge$_{0.99}$Au$_{0.01}$ and temperature at several pressures.
4. Discussion

The temperature dependence of hopping conductivity obeys the power law as shown in figure 2. On the other hand, the Mott’s VRH, hopping conduction varies according $T^{-1/4}$ law as follows:

$$\sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right],$$

(2)

where $T_0=16\alpha^3/k_B N(E_F)$, and $\alpha$ is the attenuation length for a localized wave function [1]. Fitting the experimental $\sigma(T)$ to eq.(2), the temperature coefficient $T_0$ at each pressure is obtained. With increasing pressure $T_0$ increases below 2 GPa, and decreases above 2 GPa. The pressure dependence of $T_0$ can be described as following equation:

$$\frac{d \ln T_0}{dP} = 3 \frac{d \ln \alpha}{dP} - \frac{d \ln N(E_F)}{dP},$$

(3)

As $\alpha$ may not change its value with pressure, the pressure dependence of $T_0$ is mainly caused by the pressure dependence of $N(E_F)$. Because the density of the defects in amorphous material is suspected to increase with increasing pressure [6, 7], the second term of eq.(3) may have the negative value. And so using VRH model, the increase of $T_0$ in the low pressure region cannot be explained. Furthermore the derived value of $N(E_F)$ from this model is extremely larger than the expected value from other experiments [2]. It is concluded that the VRH model is not appropriate for explaining hopping conduction in a-Ge alloys.

Shimakawa insists that in inhomogeneous media like a-Ge, electric conduction occurs by a multiphonon process [2]. On the hopping, delocalized electrons on the inner surface of microvoids couple to the phonons whose wavelength is approximately the size of the microvoids $r_C$. Its frequency is given by $\nu_0=(a_0/r_C)\nu_D$, where $a_0$ is the average lattice separation and $\nu_D$ is the Debye frequency. In MPP, as the electrons couple to long-wavelength phonons, several numbers of phonons are needed for hopping between microvoids. The number of phonons $n$ is given by $n=\Delta/\hbar\nu_0$, where $\Delta$ is the site-energy separation. The number of phonons $n$ is the same as the exponent $n$ in the power law of the temperature dependence of $\sigma$. Using these parameters, the pressure dependence of $n$ is given by

$$\frac{d \ln n}{dP} = \frac{d \ln \Delta}{dP} - \frac{d \ln a_0}{dP} + \frac{d \ln r_C}{dP} - \frac{d \ln \nu_D}{dP}.$$  

(4)

Let’s discuss the each term in eq.(4). The sum of the second and third terms is expected to be nearly zero, because microvoids are surrounded by the covalently-bonded network and $r_C$ and $a_0$ are suspected to be shortened about the same way with increasing pressure, although the number of

Figure 3. The pressure dependence of the parameter $n$ of a-Ge$_{0.99}$Au$_{0.01}$ (●). The results of a-Ge$_{0.99}$Al$_{0.01}$ [5], a-Ge [4], and a-Ge$_{0.99}$Cu$_{0.01}$ [5] are shown for reference.
pressure-induced dangling bonds increases and the bond angle deviation becomes large \cite{7}. In MPP, as the hopping occurs between the delocalized states on the inner surface of the microboids, the phonon with low frequency should play an important role. From Raman spectra measurement, the pressure coefficient of phonon frequency for TA mode with low frequency is known to decrease with increasing pressure in a-Si:H \cite{7}. Assuming that this pressure dependence of phonon frequency is also available in a-Ge alloy, the fourth term makes $n$ increase.

Now, we discuss the first and the fourth terms in two ways. Firstly, we assume $\Delta$ to be proportional to inverse of density of the dangling bonds. In this case, increase of defects with increasing pressure as reported in the photoluminescence and photoconductivity studies under pressure \cite{6, 7} cause decrease of $\Delta$. If we suppose that magnitude of $\frac{\partial \Delta}{\partial P}$ (the first term) becomes large above a certain pressure, considering $v_D$ (the fourth term) decreases monotonically with increasing pressure, it can be concluded that the increase of $n$ in low pressure region is due to the fourth term, and the decrease of $n$ in high pressure region is due to the first term. Secondary, we assume $\Delta$ correlates with band tail states rather than the states of homogeneously distributed dangling bonds because the delocalized electronic states on the inner surface of the microboids are strongly correlated with the tail states due to the large structural deviation such as deviations of bond angle and bond length. Imai et al. found that energy gap of a-Ge increases in low pressure range and decreases in high pressure range as known in crystalline Ge even in disordered materials \cite{8}. When energy gap increases, the density of states of the band tail states at the Fermi energy can be suspected to decrease in spite of the increase of the pressure-induced dangling bonds which may be homogeneously distributed in the tetrahedrally bonded network. Increase of $\Delta$ in low pressure region, and decreases of $\Delta$ in high pressure region may arise from the degree of overlap between tail states of the valence band and the conduction band. Considering that the other three terms change monotonically with pressure, the first term causes $n$ increase in the low pressure region and decrease in the high pressure region. Thus, the pressure dependence of $n$ can be explained well by the MPP model in two ways.

In figure 3, the value $n$ of a-GeV$_{0.99}$Au$_{0.01}$ and a-GeV$_{0.99}$Cu$_{0.01}$ is smaller than that of a-Ge. Because Au or Cu atoms are thought to be located inside the microvoids of a-Ge, by adding Au or Cu to a-Ge, the microvoids may be stabilized and the Au or Cu atoms may supply the movable electrons to the system. Consequently a-GeV$_{0.99}$Au$_{0.01}$ and a-GeV$_{0.99}$Cu$_{0.01}$ alloys may have the smaller value of $\Delta$ than a-Ge. That is why a-GeV$_{0.99}$Au$_{0.01}$ and a-GeV$_{0.99}$Cu$_{0.01}$ has small value of $n$.

5. Conclusion
The ac conductivity was measured up to 5 GPa in the temperature range from 77 K to 300 K, and frequency range from 20Hz to 1 MHz in a-GeV$_{0.99}$Au$_{0.01}$. Temperature dependence of hopping conductivity was well described by the power law. The change of sign in pressure coefficient of $n$ was observed at 2 GPa. This pressure dependence of $n$ agrees with the results from dc electrical resistivity experiments. Using MPP model, the pressure dependence of $n$ was well explained. It can be concluded that the mechanism of hopping conductivity in a-Ge alloys are well described by MPP.

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