Electrical oscillation in SmS induced by a constant external voltage

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We have observed a persistent voltage oscillation induced by constant external electric fields in the nonmagnetic narrow-gap semiconductor SmS. This oscillation appears with a large nonlinear conduction in a relatively low electric field of a few kV/cm. We find that the oscillation frequency clearly changes on addition of an external capacitor parallel to the sample, indicating that the oscillation does not arise from the Joule heating effect. This oscillation is analyzed in terms of a carrier charging-discharging model, which is associated with an electric-field-induced insulator-to-metal transition as proposed in the oxide insulator VO_2. This model reasonably explains the observed oscillation phenomenon, implying the existence of a possible instability toward a conductive state driven by the electric field.

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I. INTRODUCTION

Nonlinear conduction phenomena emerging in high electric fields have been observed in various materials, attracting much attention for developing potential electronic devices as well as for understanding fundamental transport properties in highly nonequilibrium states. In condensed-matter physics, the nonlinear transport has been studied in organic charge-transfer salts [1,2] and charge-density-wave materials [3]. Recently, nonlinear conduction of strongly correlated electrons has been explored both experimentally [4–10] and theoretically [11–14]. In several materials, in addition to a clear deviation from Ohm's law, an electrical oscillation against the dc input (i.e., dc-ac conversion) has also been observed. Charge-ordered organic salts exhibit a nonlinear conductivity and a characteristic current oscillation with a low frequency of ∼40 Hz, and are called organic thyristors [6]. Electrical oscillation behaviors are also reported in several correlated insulators [15–19], where nontrivial responses of correlated electrons such as an electric-field-induced insulator-to-metal transition or a collective motion of charge order are proposed to cause the oscillation. In contrast to such extensive studies in correlated organic salts and oxide compounds, on the other hand, there is no report of nonlinear transport in f-electron systems as far as we know. The f-electron materials manifest conspicuous correlation effects, and may offer intriguing features in nonlinear phenomena.

SmS is a nonmagnetic narrow-gap semiconductor with a valence state of Sm^{2+} at ambient pressure. In this compound, the $4f$ bands are largely split into $4f_{5/2}$ and $4f_{7/2}$ levels due to the spin-orbit interaction and strong Coulomb repulsion, and as a result the Fermi level is located between the occupied $4f_{5/2}$ levels and the unoccupied $5d$ bands [20–22]. This insulating phase is highly unstable against external parameters, as highlighted by a unique pressure-induced first-order insulator-to-metal transition at a critical pressure of ∼6 kbar, accompanying a distinct color change from black in the insulating phase to golden yellow in the metallic one [23]. In the metallic golden phase, the $4f$ levels lie in the expanded $5d$ bands, leading to a mixed-valence state of Sm^{2+} ($4f^6$) and Sm^{3+} ($4f^5$) configurations [24]. Recent thermodynamic [25] and optical [26] studies suggest a spontaneous condensation of excitons [27,28] as the origin of this pressure-induced phase transition. The insulating state is also susceptible to the magnetic field [29]. In contrast to conventional nonmagnetic semiconductors, a large negative magnetoresistance has been found at low temperatures [30], while its origin remains puzzling.

In this study, we have examined an electric-field effect on the transport properties in the insulating phase of SmS in a relatively low electric field of a few kV/cm. We have observed nonlinear conduction and found a characteristic voltage oscillation in a constant external voltage, which occurs in the negative-differential-resistance range. The oscillation frequency depends on the capacitance of the external capacitor, which is connected in parallel with the sample, indicating that the voltage oscillation does not arise from Joule heating. As a model of the oscillation, we propose a carrier charging-discharging process associated with an electric-field-induced insulator-to-metal transition, which is possibly related to the interband tunneling mechanism in SmS.

II. EXPERIMENT

Single crystals of SmS were grown by the vertical Bridgman method, as described in Refs. [31,32]. The physical properties of SmS are sensitive to the sample quality, and in this study, we used the single crystal of sample #9 in Ref. [32], which was prepared with a 1% excess of sulfur. Figure 1 shows the temperature dependence of the resistivity, which was measured using a standard four-probe method with a low current density. Semiconducting behavior without saturation at low temperatures is observed, as is also seen in the Arrhenius plot shown in the inset of Fig. 1, indicating that the measured single crystal is of high quality. Using the activation formula $\rho(T) \propto \exp(E_g/2k_BT)$, an energy gap of $E_g \simeq 80$ meV is evaluated, well consistent with the gap value in earlier reports [32].

For the nonlinear conduction measurement in a high external electric voltage V_E (<90 V) with a pulse width of 20 ms, we used a Keithley 6430 SourceMeter and an oscilloscope of Tektronix TDS 3012B. We constructed a series circuit consisting of the sample and a standard resistor ($R_{\rm std} = 1$ MΩ) as shown in the inset of Fig. 2(b), and measured

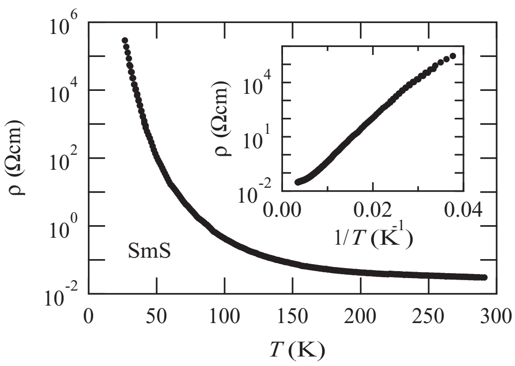

FIG. 1. Temperature variation of the electrical resistivity of SmS measured with a low current density. Inset shows the resistivity as a function of $1/T$.

the voltage of the standard resistor $V_{\rm std}$ with the oscilloscope. This measurement was conducted in a liquid-helium vessel to cool the sample at 6 K, and the standard resistor was kept at room temperature. The sample was connected to this circuit with silver paste and the contact resistance was about 50 Ω, which was sufficiently lower than the sample resistance at 6 K. The sample cross section was $A = 3.5 \times 10^{-3}$ cm^2 and the distance between contacts was $L = 0.015$ cm.

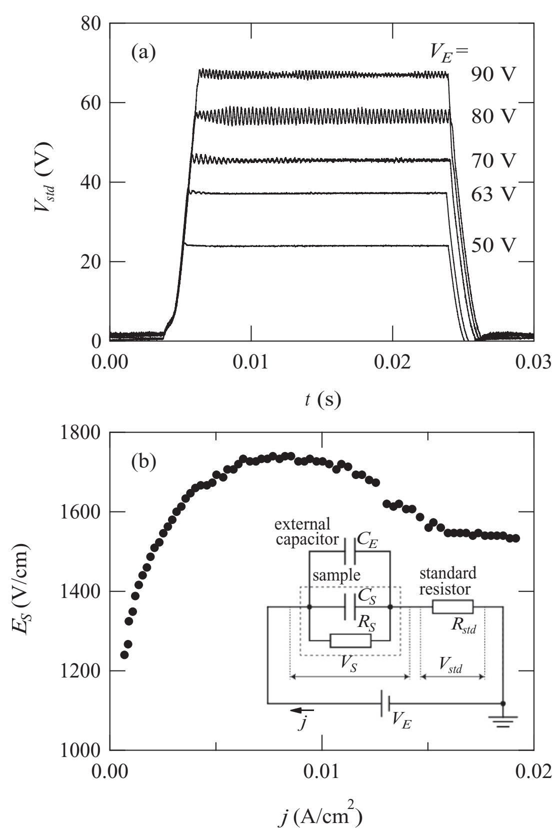

FIG. 2. (a) Voltage profiles in several external voltages with the pulse width of 20 ms measured at the external temperature of 6 K. (b) Current density dependence of the electric field on the sample. Inset shows the schematic diagram of the measurement circuit.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the time profiles of $V_{\rm std}$ measured by the oscilloscope in different external voltages V_E from 50 to 90 V at the external temperature of 6 K. We find characteristic voltage oscillations in the constant external voltage. Above $V_E = 63$ V, the voltage oscillation appears at the beginning of the pulse, and becomes large and persistent in the whole range of the pulse above 80 V. Similar voltage oscillations have been observed in the oxide insulator VO_2, which exhibits a negative differential resistance [16,17]. Thus, we depict the current density $j = V_{\rm std}/R_{\rm std}A$ dependence of the electric field $E_S = (V_E - V_{\rm std})/L$ in Fig. 2(b). In the voltage oscillation range, the average values of $V_{\rm std}$ were used. In the low external voltage $V_E < 20$ V, we cannot detect $V_{\rm std}$ with the oscilloscope, since the current is very small due to the large resistance of SmS at 6 K. A nonlinear behavior is observed in the whole measurement range, and this nonlinearity becomes striking with increasing current density. The E_S-j curve has a peak around $j = 0.008$ A/cm^2, and above this current density the voltage starts oscillating, suggesting that the voltage oscillation occurs in the negative-differential-resistance region. The electric field (voltage) at the peak position is 1740 V/cm (26.1 V), which can be regarded as a threshold field (voltage) as discussed below.

To clarify the origin of the voltage oscillation, we add an external capacitor with capacitance of $C_E = 1$, 4, and 10 nF in parallel with the sample as shown in the inset of Fig. 2(b). We then measured $V_{\rm std}$ with each capacitor in the external voltage of $V_E = 80$ V at 6 K. The sample voltage profiles $V_S = V_E - V_{\rm std}$ are shown in Figs. 3(a)–3(d). We find that the oscillation frequency decreases with increasing C_E. In addition, the oscillation wave forms become clear: The sample voltage gradually increases with time but suddenly decreases at $V_S \sim 25$ V, which is close to the threshold voltage discussed above. This behavior is similar to that observed in VO_2, which is described with a carrier charging-discharging model of a series RC circuit (R is the resistance, and C the capacitance) associated with an electric-field-induced insulator-to-metal phase transition [33].

Here we discuss the oscillation mechanism of SmS based on the model in Ref. [33]. We assume that this compound has components of capacitance C_S and resistance R_S in parallel as shown in the inset of Fig. 2(b). When the external voltage is applied and R_S is high, the carriers are charged owing to the dominant C_S component. After V_S reaches the threshold voltage V_{th}, the charged carriers are released because of the change of R_S from a high to a low value due to the large nonlinear conductivity. The origin of this nonlinearity will be discussed later. After the carrier discharge from C_S, the applied electric field on R_S decreases, and the high resistance of R_S is restored. Using the above charging-discharging process, we can roughly understand the feature of the persistent voltage oscillation in the constant external voltage.

The time dependence of the sample voltage $V_S(t)$ in each charging process is then described as

$$V_S(t) = V_0\left[1 - \exp\left(-\frac{t - t_0}{\tau_0}\right)\right], \tag{1}$$

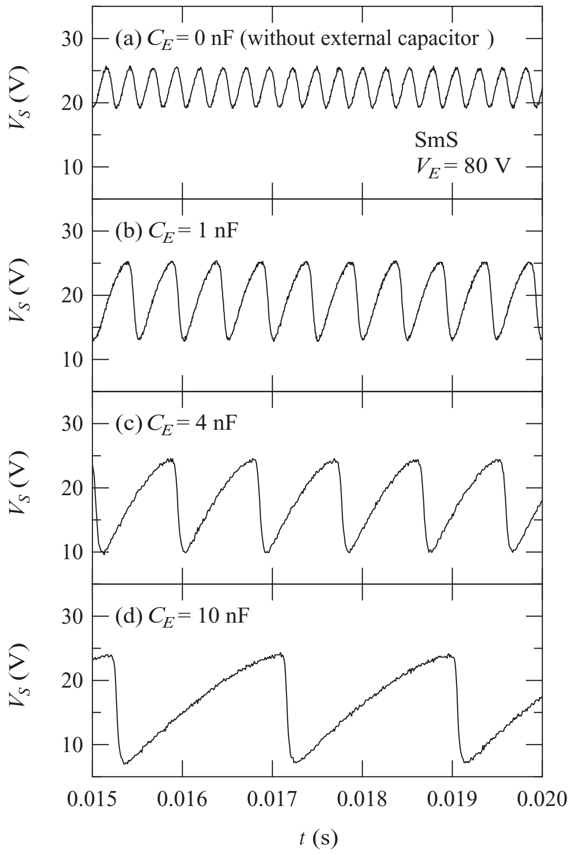

FIG. 3. The voltage oscillation profiles measured by adding an external capacitor with different capacitance values of (a) $C_E = 0$ nF (without external capacitor), (b) 1 nF, (c) 4 nF, and (d) 10 nF in $V_E = 80$ V at 6 K.

where $V_0 = V_E R_0/R_{\rm std}$, $\tau_0 = (C_S + C_E)R_0$, and t_0 is an offset time. Here $R_0^{-1} = R_S^{-1} + R_{\rm std}^{-1}$. In this case, the time constant τ_0 is proportional to $C_S + C_E$. Figure 4 displays the τ_0 obtained by fitting as a function of external capacitance C_E. As expected, τ_0 linearly increases with C_E, suggesting that the model of the charging-discharging process is reasonable to explain the mechanism of this oscillation. The finite x-axis intercept of the τ_0-C_E curve gives the value of the intrinsic capacitance of the sample $C_S \sim 2$ nF. Note that the fitting

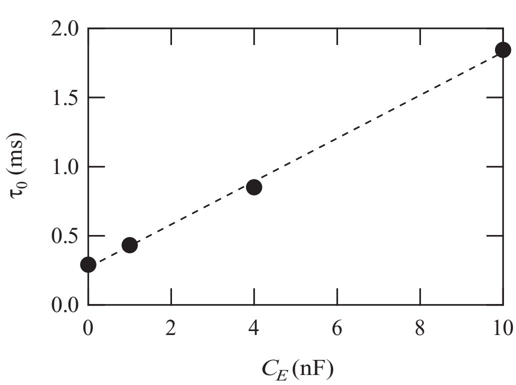

FIG. 4. The time constant τ_0 as a function of the external capacitance C_E. The dashed line represents the linear fitting result.

parameter V_0 was ∼36 V, almost independent of C_E. This leads to $R_0 = R_{\rm std}V_0/V_E \sim 0.45$ MΩ, which is close to the value of the linear slope (0.16 MΩ) in the τ_0-C_E curve. The slight discrepancy in R_0 is probably due to the simplified internal electric circuit of the sample shown in the inset of Fig. 2(b).

The oscillation amplitude of V_S also changes with C_E. Here, on addition of the external capacitor, additional carriers are charged in the external capacitor during the gradual relaxation process, and are suddenly released when the sample voltage reaches V_{th}. Thus the electrical current, which flows after the release, increases with increasing C_E owing to such additional charged carriers. The increase of release current with external capacitor leads to the increase of $V_{\rm std}$ and the decrease of V_S, which means a large sample voltage drop after the release.

Let us discuss the origin of the nonlinear conductivity causing the voltage oscillation. In this study, we apply the pulse voltage with the duration time of 20 ms, which is much longer than that of less than 1 μs in traditional nonlinear-conduction experiments [34], resulting in a substantial effect of Joule heating. The heating may lead to an oscillation in some situations. With heating, the sample temperature increases and the sample voltage decreases. The electric power in the sample may subsequently decrease, which suppresses further heating. When the electric power falls below the cooling power from the surroundings, the temperature exhibits a maximum and then decreases. This temperature decrease also causes an increase of the sample voltage and electric power. As a result, the temperature and the electric power may exhibit an antiphase oscillation as a function of time, like a hunting oscillation in a feedback circuit.

However, the external capacitance dependence of the oscillation frequency observed in this study cannot be explained only by the heating effect, because the relaxation time associated with the heating, which depends on the heat capacity of the sample and thermal resistance between the sample and heat bath, should not be changed by adding the external capacitor. In addition, the observed wave form, which is characterized by a gradual voltage increase and the subsequent sudden drop is quite different from a conventional sinusoidal oscillation. The observed wave form is rather reminiscent of the electrical oscillation found in VO_2. In VO_2, one may think that such a sudden voltage drop can be attributed to a first-order insulator-metal transition induced by the heating, while it is suggested that the persistent oscillation is not reproduced by the Joule heating only [35]. However, SmS does not exhibit a thermally driven insulator-metal transition. This means that SmS does not show the sudden carrier discharge due to the insulator-metal transition caused by Joule heating.

In some conventional semiconductors, such nonlinear conduction occurs at high electric fields of the order of MV/cm due to Zener tunneling or impact ionization. The peculiar point of present results is that the threshold field is relatively low, probably originating from the small band-gap value of $E_g \simeq 80$ meV in SmS. The threshold field in the Zener interband tunneling model is given as $\sim E_g^2/E_0ea$, where $E_0 = \frac{\hbar^2}{2m^*}(\frac{\pi}{a})^2$, e is the charge of an electron, m^* is the effective mass, and a is the lattice constant [36]. Using $a = 0.597$ nm and $m^* = 0.2m_0$ (m_0 is the free-electron mass) [23,37], the threshold is estimated to be 20 kV/cm. Although this value is still one order of magnitude larger than the observed value of $E_{th} = 1740$ V/cm, it is small enough to consider such a mechanism within the above rough estimation because the avalanche phenomenon of the tunneling electrons usually takes place below the Zener threshold field [34].

Let us compare the present result with oscillation phenomena found in other materials. In GaAs, electrical oscillation appears in high electric fields, and is known as the Gunn effect [38]. This phenomenon originates from the field-induced mobility reduction due to the peculiar band structure [39]. In the resultant current-voltage curve, the current exhibits a peak as a function of voltage, which differs from the present result. A similar wave form has been reported in charge-ordered organic salts [18,19], which may be attributed to a collective excitation of charge order in analogy to the sliding motion of density waves [3], but such an ordered state is not realized in the insulating phase of SmS. The oscillation behavior in VO_2 is proposed to be related to an electric-field-induced Mott transition [33]. Indeed, nonlinear conduction phenomena have often been seen in materials that possess instabilities toward metallic states induced by thermodynamic quantities such as temperature and pressure. In such materials, the electric field has been suggested as a nonequilibrium parameter to drive the transition [9]. While the present field-induced metalization can be understood in terms of the conventional tunneling process with a slight difference in the threshold values, SmS may possess an instability toward a metallic state, realized by electric fields in analogy to the pressure-induced insulator-to-metal phase transition [23].

IV. SUMMARY

In summary, we have constructed a series circuit of a SmS single crystal and a standard resistor, and observed a persistent voltage oscillation in constant external voltage. The voltage oscillation appears in the negative-differential-resistance region in the voltage-current curve. While the capacitance dependence of the oscillation time constant cannot be explained by Joule heating, a carrier charging-discharging model on an *RC* series circuit reasonably reproduces this oscillation phenomenon, as proposed in the oxide insulator VO_2. As the origin, we suggest that the carrier discharge arises from the decrease of the sample resistance on application of external electric fields, which seems to be related to the Zener tunneling mechanism in narrow-gap semiconductors.

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