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Electrical Conductivity of Passivated Si_2Te_3 Single Crystals[1]

By

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In honour of Prof. Dr. F. STÖCKMANN's 60th birthday

In order to obtain reliable data of the dark conductivity for Si_2Te_3 single crystals it is necessary to use samples with ohmic contacts and low conductivity surface layer. It is shown that these conditions can be met by evaporation of gold contacts after vacuum cleaving and a subsequent heat treatment, which produces a SiO_2 surface layer. The results of dc and ac conductivity measurements indicate a thermal activation of the carrier mobility parallel to the *c*-axis.

Um zuverlässige Werte für die Dunkelleitfähigkeit von Si_2Te_3-Einkristallen zu erhalten, müssen Proben mit Ohmschen Kontakten und schlecht leitender Oberflächenschicht verwendet werden. Diese Bedingungen können durch Aufdampfen von Goldkontakten nach Vakuum-Spaltung und anschließender Wärmebehandlung erfüllt werden. Die Ergebnisse von Gleich- und Wechselstrommessungen der Leitfähigkeit zeigen, daß die Beweglichkeit der Ladungsträger parallel zur *c*-Achse thermisch aktiviert ist.

1. Introduction

In the presence of water vapour a chemical reaction takes place at the surface of Si_2Te_3 crystals according to the formula

$$Si_2Te_3 + 4\,H_2O \rightarrow 2\,SiO_2 + Te + 2\,H_2Te + 2\,H_2\,.$$

As a result of this reaction SiO_2 and free tellurium is deposited on the sample surface [1]. For electrical or optical measurements on the high resistivity Si_2Te_3 it is necessary either to avoid the reaction or to restore the original low conductivity of the surface. As reported by Ziegler and Birkholz [2] sample preparation in a glove box containing dry argon gives satisfactory results in the case of photoconductivity measurements. According to Ziegler et al. [3] the conductivity of a slightly contaminated surface can be strongly reduced by a vacuum heat treatment. Both methods, however, turned out to be insufficient for sample preparation in the case of dark conductivity measurements. As the dark conductivity of Si_2Te_3 is of the order $10^{-17}\ \Omega^{-1}\ cm^{-1}$ at room temperature, the measurements are extremely sensitive to surface and contact properties.

Using Auger electron spectroscopy (AES) Erlandsson et al. [4, 5] investigated the surface layer structure of Si_2Te_3 samples after exposition to humid air and also after heat treatment in vacuum. The results for an exposed sample are reproduced in Fig. 1, a scheme of the proposed layer structure is added. According to the AES results the layer structure changes drastically with heat treatment. After a tempering process in vacuum at 600 K the tellurium is evaporated, and the remaining layer consists of SiO_2 only. It may be assumed that contacts applied to samples after such a heat treatment will show non-ohmic behaviour because of the presence of the SiO_2 layer. On the other hand, it seems reasonable to assume that this layer will protect the sample against further reaction with water, i.e. the heat treatment should produce a passivated sur-

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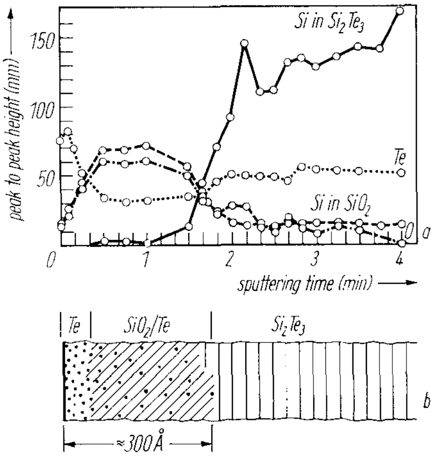

Fig. 1. Surface layer structure of a Si_2Te_3 crystal exposed to air. a) AES depth profile after Erlandsson et al. [4, 5]; b) scheme of the surface layer structure

face. In this paper methods for producing an ohmic metal contact on Si_2Te_3 are investigated, and the optimum conditions for the passivation are studied. Results of dc and a cconductivity measurements, which were performed on samples with passivated surfaces and non-blocking contacts, are reported.

2. Experimental

2.1 *Sample preparation*

Single crystals were grown by transport in the vapour phase. Platelets with area 7 to 40 mm^2 and thickness 30 to 100 μm were prepared. As mentioned before no satisfactory sample preparation was possible by using a dry argon atmosphere. A very low water vapour concentration of the order 50 ppm was sufficient to affect the surface conductivity seriously. Therefore it was necessary to perform the preparation in high vacuum. The samples were cleaved perpendicular to the c-axis. Gold contacts were applied to the cleavage planes by evaporation. The time delay between cleavage and evaporation was a few second only. The samples were then taken out of the evaporation system and transferred to the conductivity apparatus. During this transfer the samples were exposed to the laboratory atmosphere for some minutes. After vacuum tempering at 520 K for some hours inside the conductivity apparatus the samples were ready for the conductivity measurements.

To study the influence of exposition to water vapour on the properties of the contact, two samples, PZ1 and PZ2, were prepared from the same crystal using the same cleavage plane. Sample PZ1 was prepared as described before, whereas sample PZ2 was exposed to laboratory atmosphere for some seconds before the contacts were applied.

2.2 *Conductivity measurements*

Because of the very low dark conductivity of Si_2Te_3 the circuits had to be designed with good electrical isolation and low stray capacitance. The samples were mounted on a quartz plate. The electrical contact was obtained by pressing gold wires on the evaporated gold contacts. For temperature control a P.I.D. regulator was used to keep the temperature constant with high long-time stability or to obtain a linear change of temperature with time.

The dc conductivity was measured with help of Keithley electrometers 602 and 616 used in a fast-mode as a feedback-type picoammeter. In order to obtain equilibrium states the heating rate was 0.04 K/min below 470 K and 0.4 K/min above that temperature.

The ac conductivity was measured at constant temperature. In the frequency range 10^{-5} to 0.5 Hz the real and imaginary part of the conductivity were obtained by measuring current and voltage with X–Y recorder. In the range 0.1 to 100 Hz a storage oscilloscope was used. A two-channel lock-in amplifier Brookdeal 9502 with current preamplifier was applied in the range 1 Hz to 100 kHz. For all ac measurements it was necessary to control the phase shift of the instruments very carefully.

3. Results and Discussion

3.1 Passivation process

The change of the dc conductivity of some samples, which were exposed to humid air after the preparation, during a heat treatment is shown in Fig. 2. The curves a and b exhibit maxima near 400 K. It is assumed that the uppermost Te layer (Fig. 1) is evaporated in this temperature range. The curves b and c each show a second maximum near 520 K. Probably these maxima correspond to the removal of Te from the second surface layer, which consists of Te and SiO_2. After the samples had been heated above 520 K, the conductivity curves turned out to be reversible. It was also observed that samples treated in this way did no longer change their conductance when exposed to humid air. It can be concluded that a heat treatment of exposed samples results in a passivation of the surface. A scheme of the surface layer in the three stages is shown in Fig. 3.

3.2 dc conductivity

To test the contact properties, the current voltage characteristics of the samples PZ1 and PZ2 were investigated for 296 and 575 K (Fig. 4 a and b). As described before the gold contact of sample PZ1 was applied to a clean cleavage plane. This sample shows an ohmic behaviour ($I \sim U$) at low fields and space charge limited current ($I \sim U^2$) at higher fields. For sample PZ2, the gold contact of which was applied to an exposed surface, a lower conductance and non-ohmic behaviour ($I \sim U^{0.7}$) was observed at 296 K. At 575 K sample PZ2 exhibits an ohmic characteristic too, but the conductance still is reduced.

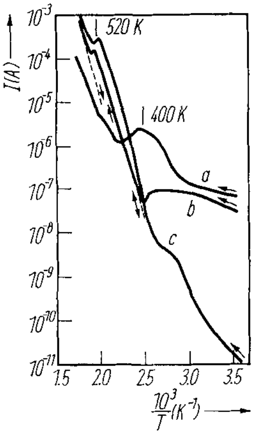

Fig. 2

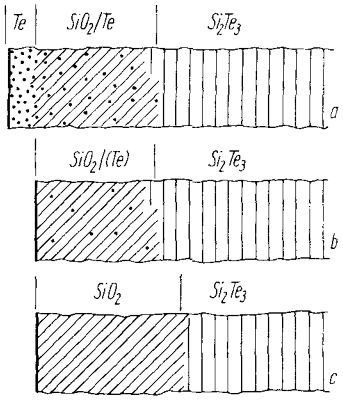

Fig. 3

Fig. 2. Conductivity changes during the heat treatment of Si_2Te_3 crystals, which had been slightly exposed to humid air. Heating rates: (a) 3, (b) 0.7, (c) 0.7 K/min. Expositions times: (a) 1 min, (b) 5 min, (c) 1 h

Fig. 3. Scheme of the surface layer structure of Si_2Te_3 crystals a) after exposition to humid air for some weeks, b) after 2 h heat treatment of the exposed sample at 500 K, c) after 4 h heat treatment of the exposed sample at 650 K

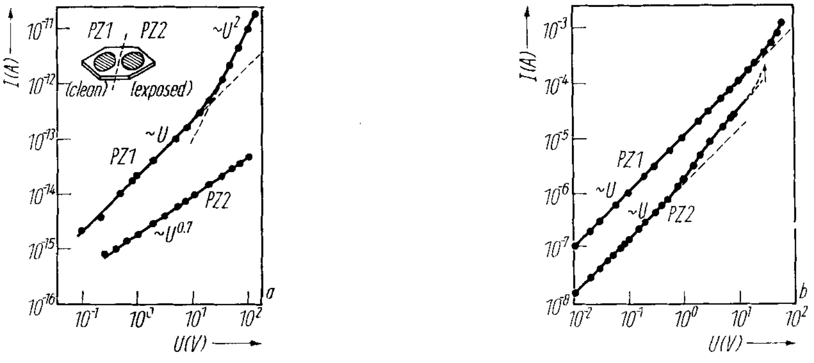

Fig. 4. Current–voltage characteristic of Si_2Te_3 at a) 296 K and b) 575 K (parallel c-axis). PZ1: ohmic behaviour, PZ2: non-ohmic behaviour

The temperature dependence of the dc conductivity parallel to the c-axis of samples PZ1 and PZ2 is shown in Fig. 5. The data for sample PZ1 will be discussed only. The activation energy of the conductivity is 1.04 eV below 620 K and 1.43 eV above 620 K. As shown in [2] the hole mobility parallel to the c-axis is very low ($\mu_{\|} \approx$ $\approx 2 \times 10^{-3}$ cm^2/Vs at 283 K). Therefore, it may be concluded that the observed activation energy of the conductivity has its origin both in carrier activation and an activated mobility $\mu_{\|}$ due to a hopping process. Assuming that intrinsic conduction is dominant above 620 K and using a value for the band gap $E_g = 2.2$ eV (1), an activation energy of the mobility $E_\mu \approx 0.3$ eV can be estimated. Therefore, below 620 K the carriers (holes) are assumed to be activated from deep impurity levels lying 0.7 eV above the valence band. This result is in good agreement with data obtained from the analysis of thermally stimulated currents. The corresponding experiments were performed by cooling the crystal with a voltage bias applied and subsequent heating without bias.

At a certain electrical field strength parallel to the c-axis switching effects have been observed. An example is shown in Fig. 6. The switching takes place from a high resistivity to a low resistivity state. If the voltage is reversed the opposite effect occurs. It has not yet been established whether the transition is controlled by traps or by ionic conduction due to the defect structure of the lattice.

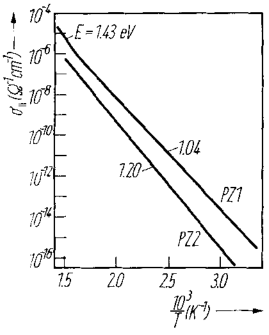

Fig. 5. Temperature dependence of the dc conductivity of Si_2Te_3 (parallel c-axis)

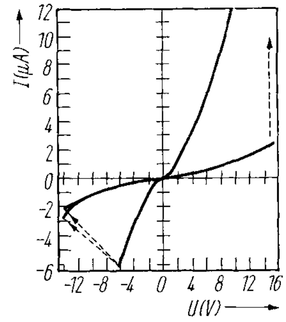

Fig. 6. Switching characteristic of a Si_2Te_3 device (430 K)

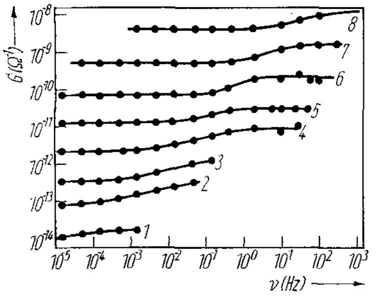

Fig. 7

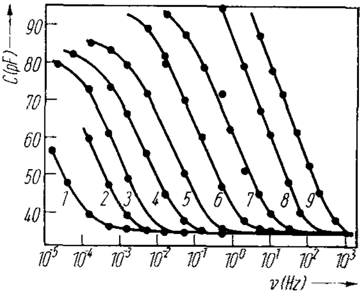

Fig. 8

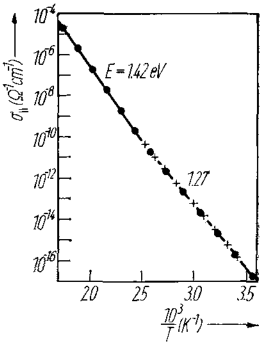

Fig. 9

Fig. 7. Frequency dependence of the real part of the electrical conductance G of Si_2Te_3 at different temperatures (parallel c-axis, Li doping). (1) $T = 294$, (2) 307, (3) 317, (4) 331, (5) 346, (6) 361, (7) 378, (8) 397 K

Fig. 8. Capacity of Si_2Te_3 versus frequency at different temperatures (parallel c-axis, Li doping). (1) $T = 294$, (2) 307, (3) 317, (4) 331, (5) 346, (6) 361, (7) 378, (8) 397, (9) 415 K

Fig. 9. Temperature dependence of the dc conductivity (———) of Si_2Te_3 (parallel c-axis, Li doping + indicates extrapolated dc conductivity from Fig. 7 $\left(\lim\limits_{\omega\to 0} \sigma(\omega)\right)$

3.3 ac conductivity

Real and imaginary part of the electrical conductance of Si_2Te_3 doped with Li is plotted versus frequency in Fig. 7 and 8. The real part of the conductivity increases with frequency approximately by a factor 2. The characteristic frequency for this process increases exponentially with temperature. An activation energy of 1.27 eV is obtained. Further investigations are necessary to decide whether traps or ionic conduction contribute significantly to the observed effects.

The temperature dependence of the dc conductivity for Li-doped Si_2Te_3 is shown in Fig. 9. The activation energy in the extrinsic range is enhanced by Li-doping. As indicated the extrapolated dc conductivity data from Fig. 7 are in good agreement with these results.

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