# PROPERTIES OF EVAPORATED TELLURIUM FILMS

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(Received June 15, 1955)

## 1. Introduction

The writer has recently been engaged in the investigation of the properties of bolometers prepared by vacuum evaporation. As a bolometer of large temperature coefficient of electrical resistance posseses high sensitivity, it is clearly advantageous to make bolometers of semiconducting material. Among the semiconductors tellurium is especially suitable for an evaporated bolometer, because its low melting point can make evaporation easy and because it, not being a chemical compound, does not decompose during evaporation. For this reason tellurium was first adopted in order to produce sensitive evaporated bolometers. The problem is, however, much more complicated than expected, because the evaporated tellurium film shows unusual behaviour. As such a film is considered to be a representative of the evaporated films of semiconductors, the experimental results concerning its various properties will be summarized in this paper.

When a substance is evaporated onto a surface in vacuum, atoms (or molecules) which have collided with the surface move about on it for a while and, losing their energy rapidly, are finally settled at stable positions. If the surface temperature is sufficiently high during this period, they can move about for a compartively long time to reach the true stable positions and to make large crystals. The crystals formed under such conditions are almost perfect and their sizes are fairly large. On the other hand, when the surface temperature is low, the atoms are soon brought to rest and fixed at metastable positions before they can reach stable ones (Abschreckende Kondensation). There are many defects and distortions in these crystals, and the sizes of the crystallites are rather fine. Such thin films, therefore, would exhibit peculiar properties different from those of bulk crystals. In fact, Niebur[1)] found an anomalous behaviour of the thin film of tin evaporated on a surcace which was kept at an extremely low temperature (20° K). These films show very high electrical resistance directly after evaporation and its variation with temperature is irreversible so long as the temperature is not raised sufficiently high. But when the film is brought into room temperature, its anomalous properties dissapear and the resistance versus temperature curve coincides with the ordianry one. Such anomalies become less remarkable as the temperature of the surface during evaporation approaches room temperature. These facts indicate that there are many lattice defects and distortions in the thin film condensed on the cold surface, which are extinguished gradually with the increase of temperature, and at the same time the crystals grow larger and larger. The metals are liable to crystalize so that the ordinary metal film condensed on a surface at room temprature contains comparatively little lattice defects and the size of crystals is farely large, whence these anomalous phenomena are seldom noticed under ordinary conditions. According to Sakurai,[2] however, the tellurium film condensed on a quartz plate shows a similar anomalous behaviour. This anomaly disappears after the film is annealed at about 200°C, and the properties come to resemble to those of bulk tellurium. Furthermore, if tellurium is evaporated on a surface kept at a temperature higher than 200°C, the irreversible temperature variation can be observed no more. As the properties of evaporated film are dependent on that of substrate, investigations were carried out in our laboratory with the tellurium film condensed on the collodion mumbrane.

## 2. Experimental Results

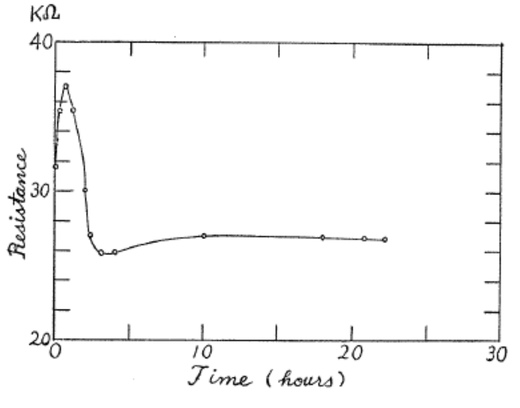
To make the collodion membrane, its solution in ether is spread on a plate of glass, and a frame which is to support the membrane is pressed on it before the mumbrane becomes perfetly dry. Then, it is stripped off the glass with a pair of tweezers carefully so that it may stick to the frame tightly and no wrinkles may be caused. The membrane thus prepared is stretched with considerable tension and proves to be very strong. From the interference colour, its thickness seems to be comparable with the wavelength of light.

If a block of metal is placed close to the back of the collodion membrane, the temperature of the membrane remains comparatively low during evaporation. This is a kind of "Abschreckende Kondensation." On the contrary, if the block of metal is dismissed and the membrane is heated during evaporation, the properties of the condensed film is quite different from those in the former case.

In the following these results will be described in detail.

### A. The membrane is cooled during evaporation

*1) The variation of electrical resistance with time*



The resistance increases rapidly immediately after the specimen is taken out of the vacuum apparatus, and then decreases soon and becomes nearly constant after twenty or thirty hours (Fig. 1). Almost all the specimens show the similar tendency, but the resistance of a few increases monotonously to reach the final value.

FIG. 1. Area : $4 \times 10\ \text{mm}^2$
Thickness : 120Å

*2) Variation with temperature.*

The change of resistance with temperature is not reversible and rather complicated. Examples are shown in Figs. 2 and 3. The resistance decreases first with increase of temperature, and when after this temperature is lowered the resistance increases through another path different from the former. Temperature being raised again, it decreases through nearly the same path, but temperature being lowered for the second time, it increases through another different path. This can be repeated many times, and the resistance seems to increase ultimately by these processes. (If the specimen is heated above 60°C, the collodion film becomes deteriorated.) This tendency is more remarkable with increase of the film thickness. (Compare Fig. 2 with Fig. 3.)

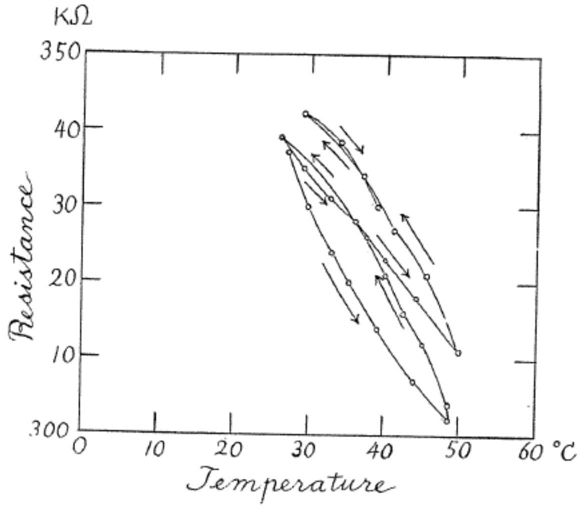


FIG. 2. Area : 0.2 × 8 mm.
Thickness : 1300 Å.

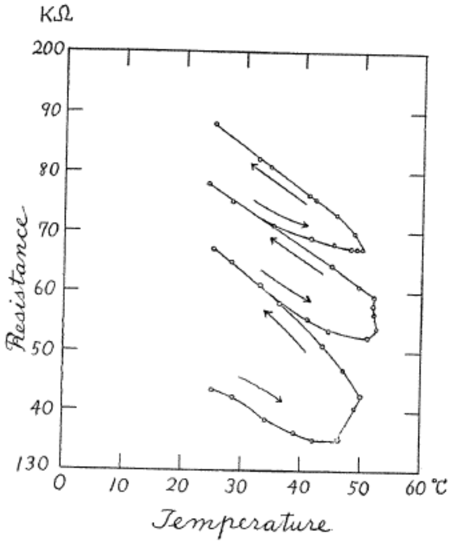


FIG. 3. Area :0.2 × 8 mm.
Thickness : 2600 Å.

*3) Variation with humidity*

If the specimen is inserted into a decicator, the resistance decreases remarkably (about 30%). After it is exposed to the air again, the resistance assumes about the same value as before. This may be caused by the expansion of the collodion film by assorbing water vapour. The difference seems to be, however, too large to be explained on this simple assumption, although, considering that the surface of collodion film is not perfectly flat, but is very rough microscopically, and the tellurium film is composed of discontinuous microcrystals, this assumption is not necessarily impossible.

*4) Current noise*

A fairly large amount of noise is generated in these evaporated tellurium films when electric current is passed through them. Those films which is thinner than about 1000 Å give rise to nearly the same amount of noise, and this noise seems to be independent of heat treatment. On the other hand, when the thickness becomes of the order of 2000 Å, the film shows a remarkable increase of noise. It is not unlikely that this phenomenon is in some relation to the growing of microcrystals.

### B. The membrane is not cooled during evaporation

*1) Variation with time*

The electrical resistance seemes to decrease slightly after evaporation, but this is not so conspicuous as in the case A.

2) *Variation with temperature*

There remains a little irreversible change with temperature as is shown in Fig. 4, though the hysteresis is not so pronounced as in the case A. This hysteresis cannot be extinguished even if heating and cooling is carried out repeatedly. If the specimen is bombarded with electrons of several hundred volts the hysteresis becomes much less remarkable.

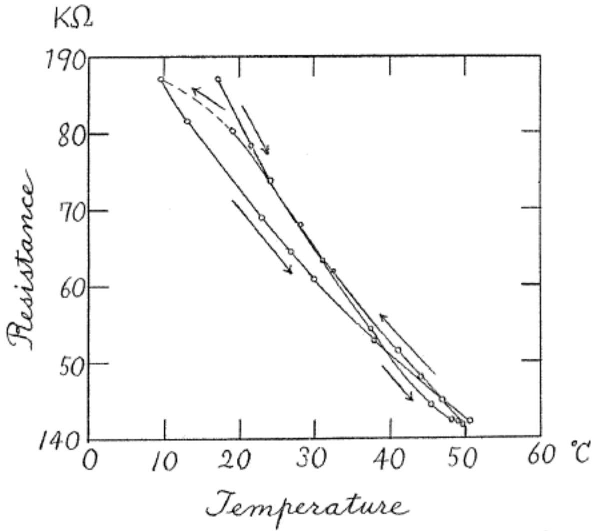


FIG. 4. Area : 0.2 × 10 mm. Thickness : 3900 Å

3) *Variation with humidity*

There can be seen little or no change of resistance with humidity in this case.

4) *Current noise*

An evaporated film with the thickness of several hundred Angstroms, shows nearly as much current noise as those films of the same thickness in the case A, and this noise is independent of heat treatment. If the thickness attains to about 1000 Å, the noise is considerably smaller than in the case A. A sudden increase of noise, however, occurrs when this film is annealed at about 50°C, and as a result of this the specimen becomes quite inadequate to the bolometer. If the film thickness exceeds about 2000 Å, it shows already a large amount of noise directly after evaporation. Annealing at about 50°C or bombardment with electrons of several hundred volts does not seem to have any effect on the amount of current noise.

### 3. Discussion

The above results indicate that the structure of the evaporated tellurium film is considerably complicated. For other metals, *e.g.* bismuth, the hysteresis of the variation of resistance with temperature and the current noise tend to decrease with increase of the film thickness. This is perhaps because the evaporated film becomes stronger and more stable as the film thickness increases, and is able to withstand the deformation of substrates caused by absorbing of water vapour or by other reasons. On the contrary, there can be seen no such tendency for tellurium films, and furthermore thicker films give rise to much more current noise than thinner ones. Although these anomalous phenomena permit no simple explanation, yet they seem to be in close relation to the brittleness of tellurium and its crystal structure. As the electron diffraction patterns of both thin and thick films exhibit typical sharp rings, (an example is shown in Fig. 5) the evaporated films seem to be in a highly crystalized state and not amorphous. (There is little possibility of recrystalisation caused by the bombardment of electron beam during exposure because the beam intensity is very small). Hence, the instability of the tellurium film seems to arise from the instability of the assemblage of microcrystals and not from the imperfect structure of the micro-crystal itself.

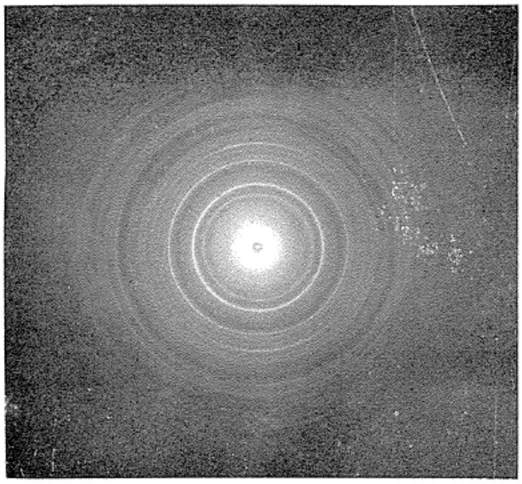


FIG. 5.

Comparing the current noise of tellurium film with those of other metals, one must assume that there are two kinds of current noises. First, as the comparatively thin evaporated films is not continuous, but composed of many isolated islands, the conduction of electrons through the film is subjected to considerable disturbance, which is the origin of the current noise. The noise of very thin tellurium film is to be regarded as of this type. This type of noise must decrease as the film thickness increases, because the distances of the islands become smaller. This tendency is actually observed, and is especially clear for bismuth. Secondly, when the electric current is passed through a film which is irregular and unstable like the tellurium film, another kind of noise is generated even if the film is so thick that the islands are in contact with each other. This noise of unkown origin is by far more remarkable than that of the first kind.

In conclusion, the tellurium film evaporated on a collodion membrane is not in a stable state and possesses no definite properties without some after-treatment. But if one wants to bring the film in a stable state, one must make such a violent heat treatment (or electron bombardment) as would destroy the membrane of collodion.

For this reason, tellurium is not a good material for the evaporated bolometer which is to detect small intensity of radiation, though its temperature coefficient of electrical resistance is about ten times as large as those of ordinary metals.

## 4. Acknowledgement

The author wishes to express his appreciation to Prof. T. Suga for his kind guidance throughout the investigation and to Mr. Y. Fukano for his helpful assistance and stimulating discussions.

## Literature

1) J. Niebur : Z. Phyik, **132**, 468, 1952.
2) T. Sakurai and S. Munesue : Phys. Rev., **85**, 921, 1952.