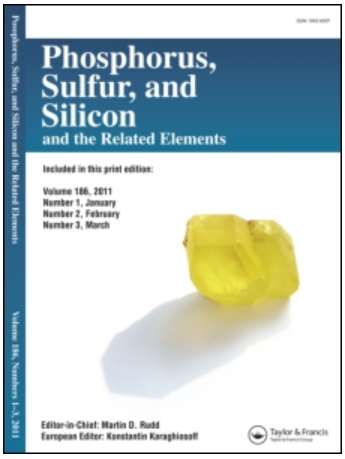

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Champness, Clifford H. and Pan, Jin(1988) 'STABILITY OF *Se - Tl* SCHOTTKY JUNCTIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 38: 3, 399 — 407
To link to this Article: DOI: 10.1080/03086648808079734
URL: http://dx.doi.org/10.1080/03086648808079734

Phosphorus and Sulfur, 1988, Vol. 38, pp. 399–407
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STABILITY OF $Se - T\ell$ SCHOTTKY JUNCTIONS

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Abstract Evaporation of thallium on a crystallized layer of selenium results in an excellent Schottky diode, exhibiting a forward-to-reverse current ratio at 1 volt of some four to five orders of magnitude and a forward ideality factor close to unity. However, with the passage of time, there is a degradation in these electrical characteristics, if the thallium is exposed to the atmosphere, even at room temperature. The observed changes are a progressive increase in series resistance and a decrease in parallel capacitance. However, the changes with time can be greatly reduced if the thallium is covered with an evaporated film of Wood's metal. X-ray diffraction analysis of films of thallium deposited on glass substrates, shows that after prolonged exposure to air, the film is progressively transformed into $T\ell_2CO_3$. Oxide formation is only apparent after storage in oxygen, rather than air. The electrical degradation in the diodes is thus the result of atmospheric conversion of metallic thallium into the less conducting carbonate.

INTRODUCTION

During the period that the selenium rectifier was actively used as an electrical device, several decades ago, it was found by the manufacturers that a small addition of thallium to the counterelectrode alloy (often of cadmium and tin) resulted in improved performance of the device in the reverse direction. While much study was made at that time of the effect of thallium in the selenium and in the counterelectrode[1,2,3], there is no record in the literature of a device fabricated with thallium alone as the counterelectrode. Thallium has a relatively low work function of about 3.8 volt[4], while selenium has the highest work function among the elements, with a value of 5.9 volt[5]. Thus, by the simple rules for an ideal Schottky junction (i.e. negligible interface states), a contact between the two elements should have a barrier height of reasonable value. Accordingly, $Se-T\ell$ diodes were prepared in our laboratory for study. These devices showed excellent rectification with a forward-to-reverse current at 1 volt of four to five orders of magnitude and a forward current having a dependence of the form exp[eV/(nkT)] over several decades, with an ideality factor n near unity. Here, V is the voltage, T is the absolute temperature, e the electronic charge and k is Boltzmann's constant. It was found that the rectification performance was reduced rapidly, if the device was heated after fabrication, even in the inert atmosphere of nitrogen. As a result of electrical studies[6], this was ascribed to the formation of $T\ell Se$ at the $T\ell/Se$ interface. However, in addition to this, it was also found that degradation in the electrical rectification occurred from simply storing the device in the atmosphere at room temperature over periods of days or weeks. The present study was therefore undertaken to characterize these electrical changes in the $Se - T\ell$ diode

with storage in air and offer an explanation of the cause.

FABRICATION OF $Se - Tl$ DIODES AND MEASUREMENTS

The diodes for study were structures of the form $Al - Bi - Se - Tl-$ Wood's metal. Each device was prepared on a base consisting of a short cylinder of aluminum with flat end faces, one of which was lapped to produce a surface sufficiently rough to ensure good adhesion of the subsequently deposited films. Following this, a thin film of bismuth was deposited and then a film of selenium, thickness about 20 microns, by evaporation. During the Se deposition, the substrate was maintained at a temperature of $135^{o}C$ to crystallize this element into the trigonal form and, at the same time, to reduce the electrical resistance at the Bi/Se interface. The Se used, contained about 60 ppm of chlorine. Next, a thin film of thallium was evaporated on the selenium through a metal mask containing four circular holes of equal size (0.143 cm^2). On top of these four Tl areas, Wood's metal (an alloy of 50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd) was evaporated through a metal mask with four circular holes of unequal size; these areas were A1 = 0.143, A2 = 0.063, A3 = 0.034 and A4 = 0.016 cm^2 and are schematically indicated in the inset to Fig. 1. A fine copper wire was then soldered to each of these areas with Wood's metal, with the aluminum base serving as the other common electrode.

Immediately after fabrication of a structure, electrical measurements were made on each of the four Tl areas. These consisted of static point-by-point measurements of current as a function of voltage in the forward and reverse directions, incremental parallel capacitance and resistance measurements as a function of frequency between 100 Hertz and about 4 MHz at zero bias.

RESULTS OF ELECTRICAL MEASUREMENTS ON DIODES

Fig. 1 shows a plot of current density against voltage on semilogarithmic scales for the four different thallium areas of a typical $Se - Tl$ sample, JP 36. The results for the freshly-made sample show forward characteristics, which are almost the same for all four of the different Wood's metal areas. It is also to be noted that, at this time, the forward current was almost five orders of magnitude greater than the reverse current.

The open symbols, linked by broken lines in Fig. 1, show results after 40 days of storing the sample in the laboratory at room temperature and the solid symbols, linked by continuous lines, show results after 138 days. The decrease of current density in the forward direction as a result of storage is clearly apparent. It is also to be noted that the decrease of current increased inversely as the area of Wood's metal over the Tl. The fact that the decreases of current were much smaller at low voltage suggests that the changes were due to an increase in series resistance of the diodes. Changes in the reverse characteristics were not clear and are not shown.

Fig. 2 shows the variation of incremental capacitance, C_p, with frequency for the same $Se - Tl$ sample. For the freshly- made sample, C_p decreases rather slowly with frequency until about 10 kHz, after which the fall is more rapid and then it tends to a plateau as 1 MHz is approached. An explanation for this form of variation has been given previously[7]. At this stage, there was little variation of C_p between the different Wood's metal areas. However, after storage of the device for 10 and 40 days, the capacitance decreased to the values shown for the three smaller areas A2, A3, and A4. In the case

of area A1, where the Wood's metal completely covered the $T\ell$, no decrease occurred. After 138 days, C_p decreased further, even for area A1. Fig. 3 shows a plot of C_p versus Wood's metal area A_w for two frequencies after 40 and 138 days. It is clearly seen that C_p increased with increase of A_w, with near-linearity at 1 MHz after 40 days. Thus, after aging in air, the capacitance was determined, no longer by the original thallium area, but by the area covered with Wood's metal.

The variation of incremental resistance R_p with frequency is shown in Fig. 4 for the same sample. It is seen for the freshly-made sample that R_p remained essentially constant with increasing frequency up to about 1 kHz, after which it decreased steadily, with an inflection point between 10 and 100 kHz. The R_p values at this stage were almost the same for the four areas. After 40 days (the values were about the same after 10 days), the R_p values at lower frequency are seen to have decreased for the three larger Wood's metal areas. However, since the fall-off of R_p with frequency was less steep than the curve for the freshly-prepared sample, the values at higher frequency were larger for all the areas. After 138 days, the R_p values were larger at all frequencies. It may be noted that at any given frequency the resistance increased with decrease of A_w. Fig. 5, where R_p is plotted against A_w on log-log scales, shows that this decrease was nonlinear.

THALLIUM DEPOSITED ON GLASS

The changes in the electrical characteristics of the $Se - T\ell$ diodes with storage time in air suggested reaction of the thallium with the atmosphere. Accordingly, a thin film of metallic thallium was vacuum-deposited on a glass microscope slide, which had already been coated with two stripes of gold. Using the gold areas as electrodes, the resistance of the deposited film was measured over the course of several days and the result is shown in Fig. 6. It is noted that the resistance increased first slowly and then more rapidly, so that it was greater than $1M\Omega$ after 90 hours, beyond which it was too high to measure easily. Initially, the deposit was bright, shiny and opaque but after several days, it became whitish-brown in colour and was almost translucent.

It was at first presumed, after referring to literature on thallium[8], that the observed changes were due to atmospheric oxidation of the film. To check this, therefore, Debye-Scherrer X-ray diffraction peaks were recorded from a freshly-prepared and from an air-aged film, using copper $K\alpha$ radiation. The lines as a function of twice the deflection angle are indicated in Fig. 7a for a freshly-deposited film; as expected, the peaks correspond to metallic thallium. Fig. 7b shows the peaks from a film after 37 days of storage in air. It is seen that these peaks correspond to $T\ell_2CO_3$ and not to the lines for the oxides of thallium. Since normal air is reported to contain about 0.03% of CO_2[9], this result came as a considerable surprise. The experiment was therefore repeated, with the same result. A further experiment was then carried out in which a freshly-prepared thallium film on glass was stored for two days in oxygen and heated at the same time at a temperature of 70 to 80°C to accelerate the reaction. The diffraction lines for this sample, shown in Fig. 7c, indicate only lines due to $T\ell_2O_3$ and $T\ell_4O_3$ but not $T\ell_2O$. Thus the oxides were formed only when the other components of normal air were not present.

DISCUSSION OF RESULTS

The X-ray diffraction results indicate that the deposited thallium in normal air is progressively converted to the carbonate rather than the oxides. While water vapour, may be suspected to play a role in this process, no further experiments were done to determine the mechanism involved.

The conversion from a metal to a non-conductor is thus the cause of the increase of series resistance of the diodes with storage time. This also explains the decreases of capacitance, at least over the 40 day period. Thus, the thallium not covered with the Wood's metal film is converted to the insulating carbonate (Fig.8), leaving the capacitance to be determined only by the area of the Wood's metal itself. This result and the fact that the capacitance of area A1 did not decrease during the 40 days, indicate that the Wood's metal acted as an effective barrier against atmospheric attack. However, the further decrease of capacitance with the longer exposure time, which occurred even for area A1, suggests atmospheric attack possibly at the edges and underneath the Wood's metal film.

The changes in incremental resistance with time are more difficult to interpret. This is especially the case for the first 40 days at low frequency, where R_p decreased for the three larger areas of Wood's metal. However, in this frequency range, the R_p values are likely to correspond more to the resistance of the depletion layer and thus could be affected by thallium diffusing in as a dopant. At higher frequencies, however, R_p corresponds more to the bulk of the selenium and so it would then increase with time due to the confinement of current flow to just the area of the Wood's metal by the transformation of the unprotected thallium into the carbonate. For the longer storage time, extension of the process would lead to increases of R_p at all frequencies .

CONCLUSIONS

The present study shows that, although thallium deposited on crystallized selenium makes an excellent rectifying diode, its electrical characteristics degrade with time if the device is left in the atmosphere, due to progressive conversion of the uncovered thallium into its carbonate. However, a covering of the thallium by a metal film, that does not react with the atmosphere, greatly reduces the degradation by acting as a barrier to attack. While determination of the preferential carbonate reaction would be an interesting study, it lies outside the scope of the present investigators.

ACKNOWLEDGEMENT

The authors would like to acknowledge the support of this work by the Natural Sciences and Engineering Research Council of Canada.

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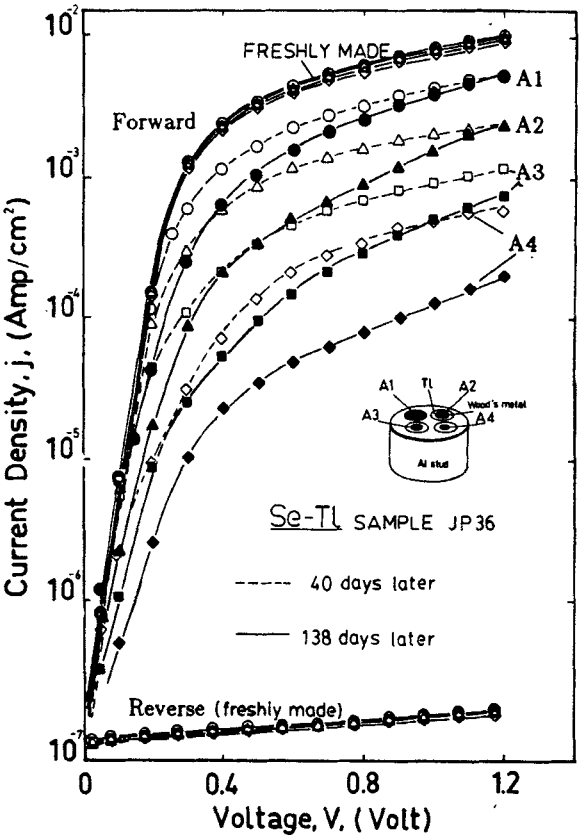

Fig.1 Current density as a function of voltage for the four areas of a Al-Bi-Se-Tl-Wood's metal structure as measured when freshly made and after periods of storage in air of 40 and 138 days.

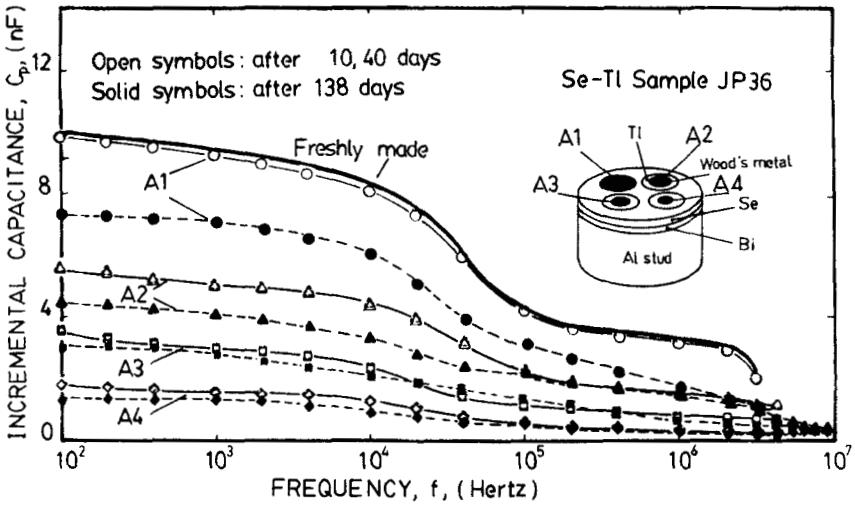

Fig.2 Incremental parallel capacitance at zero bias as a function of frequency for the four areas of a Al-Bi-Se-Tl-Wood's metal structure, as measured when freshly made and after storage in air for periods of 10, 40 and 138 days.

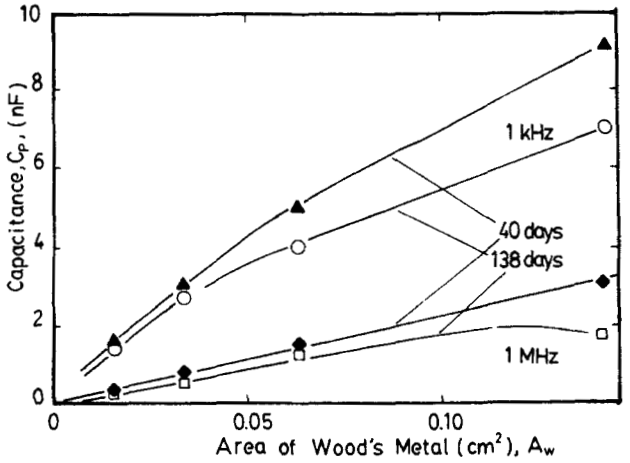

Fig.3 Plot of incremental capacitance against A_w, area of Wood's metal film, at frequencies of 1kHz and 1MHz on a Al-Bi-Se-Tl-Wood's metal structure after storage in air for 40 and 138 days.

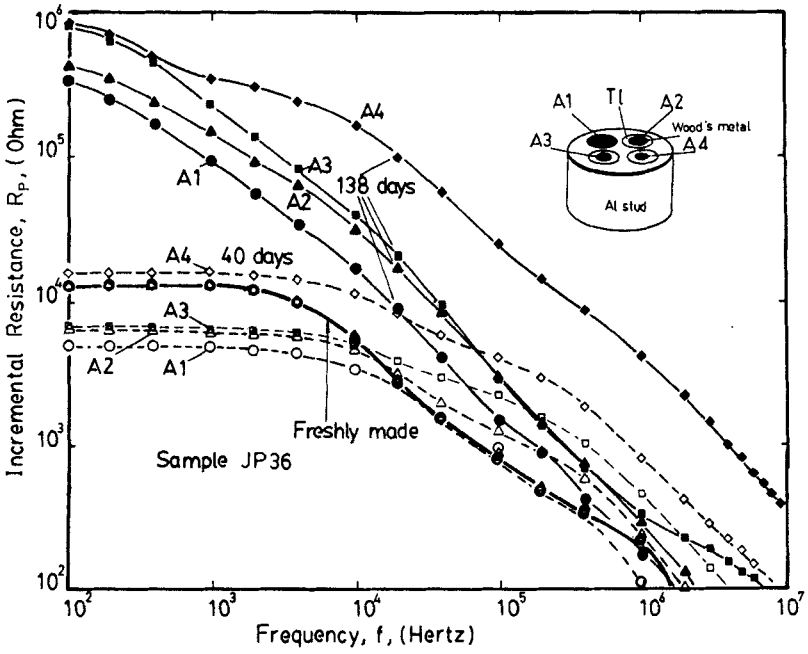

Fig.4 Incremental parallel resistance at zero bias as a function of frequency for the four areas of a Al-Bi-Se-Tl-Wood's metal structure, as measured when freshly made and after storage for periods of 40 and 138 days in air.

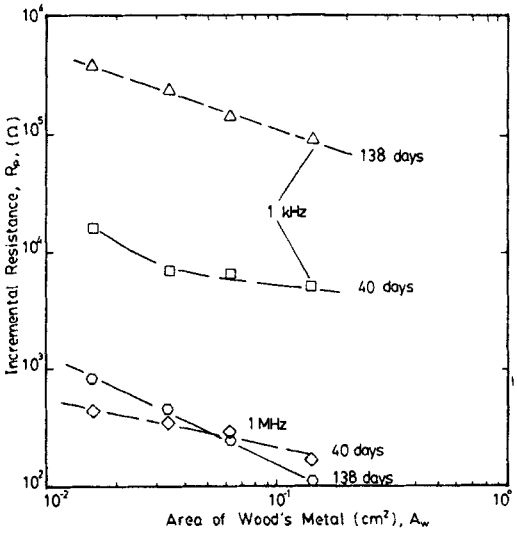

Fig.5 Plot of incremental resistance against A_w, area of Wood's metal film, at frequencies of 1kHz and 1MHz on a Al-Bi-Se-Tl-Wood's metal structure after storage in air for 40 and 138 days.

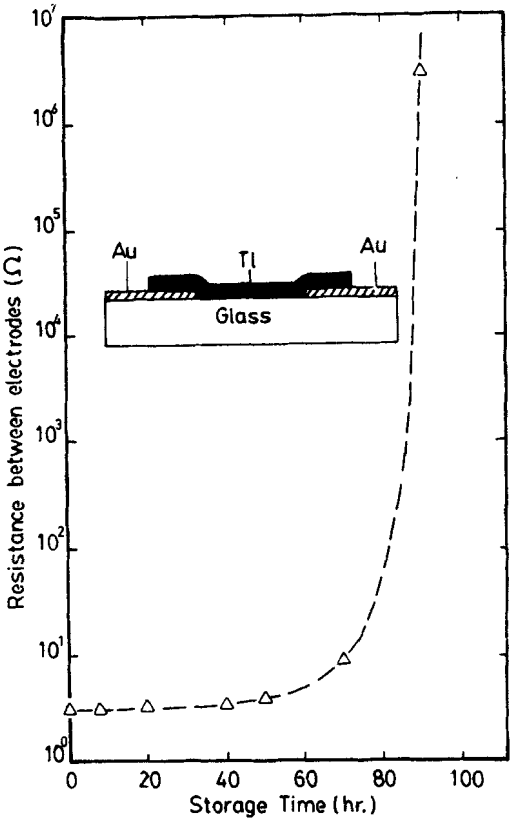

Fig.6 Electrical resistance plotted against storage time in air for a film of thallium deposited on glass.

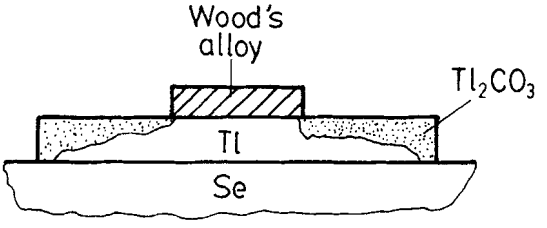

Fig.8 Schematic cross-section of a Se-Tl diode postulated after partial atmospheric conversion of the thallium to Tl_2CO_3.

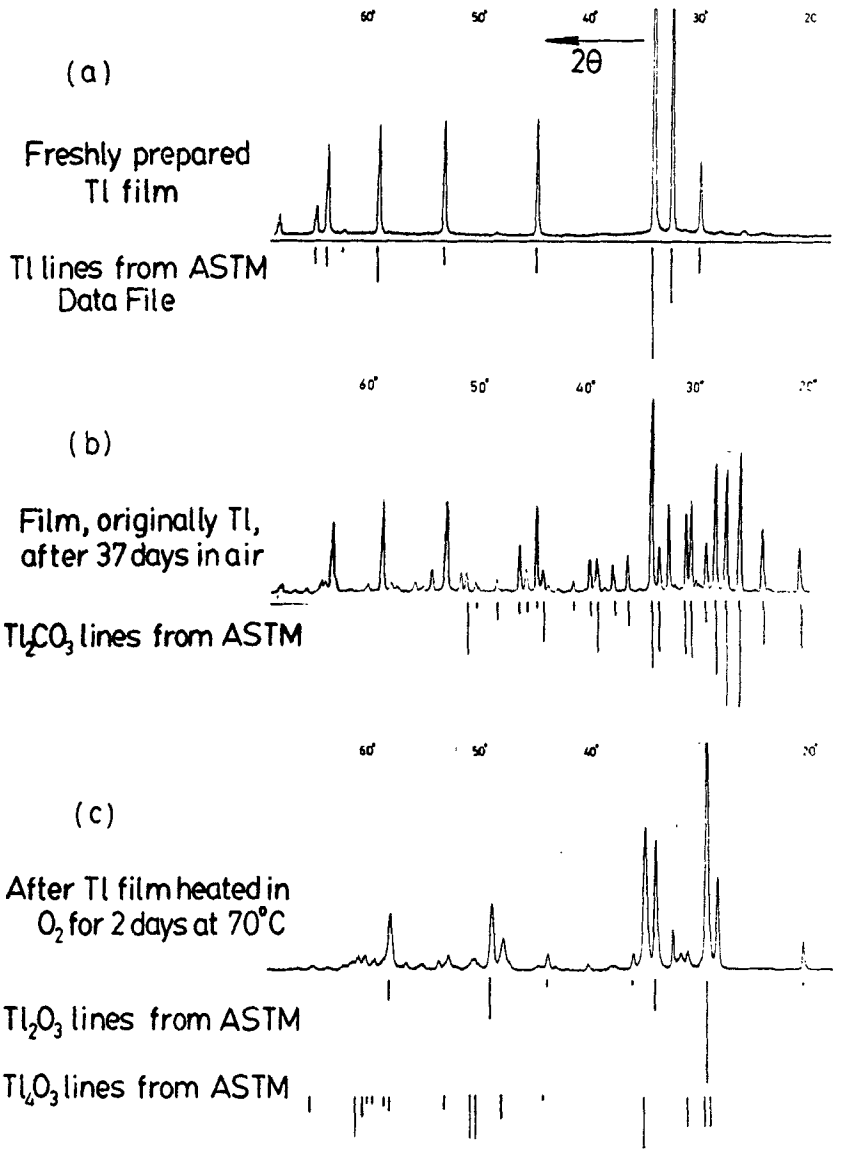

Fig.7 Debye-Scherrer X-ray diffraction intensities (Cu-Kα) as a function of twice the deflection angle for films originally of thallium deposited on glass.