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***In situ* electrical resistivity measurements during the sulphuration of pyrite and Fe thin films**

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Abstract. A cell has been built to measure the electrical resistivity of single crystals and thin films in a sulphur atmosphere. Resistivity variations during the sulphuration of pyrite samples have been investigated as a function of temperature (~ 450 – 723 K) and of time at constant temperature. The transformation of Fe thin films into pyrite films has been followed through their electrical resistivity changes up to ~ 623 K. Results are briefly discussed by considering the stoichiometric and crystallographic transformations undergone by the films. After these preliminary results some open questions are presented.

1. Introduction

Pyrite thin films have been produced in several laboratories using different techniques in the last few years. Their properties (structural, morphological, optical, composition depth profiles etc) have been investigated by several authors [1]. In particular, electrical characteristics (resistivity, Hall mobility, carrier density) have been studied [2–11] and it has been found that they are greatly dependent on the experimental procedure used to prepare the films. Their electrical resistivity has been measured at room temperature or lower [5, 7–9, 11] but as far as we know no study has yet been made dealing with the behaviour of that parameter on heating the pyrite thin films. On the other hand, growth of pyrite films by sulphuration of thin Fe films has been accomplished by a few groups [5, 7, 12, 13] but virtually no information is available yet on the characteristics of the films during the sulphuration process itself.

In this paper we deal with these problems by using a cell specially designed to work in sulphur atmosphere. The influence of a thermal sulphuration of the pyrite thin films on their resistivity has been studied at temperatures between 450 and 723 K. The film resistivity suffers significant variations, which are discussed in terms of plausible changes in their crystallization and stoichiometry as proposed in a previous paper [11]. The formation of a pyrite film by sulphuration of an Fe film is accompanied by an abrupt increase of the electrical resistivity at temperatures ~ 600 – 623 K. This behaviour is compared with that shown by other similar dichalcogenides.

2. Experimental procedure

Electrical resistivity measurements have been made by applying the Van der Pauw method [14] to different types of sample placed into the closed cell drawn in figure 1(a), which

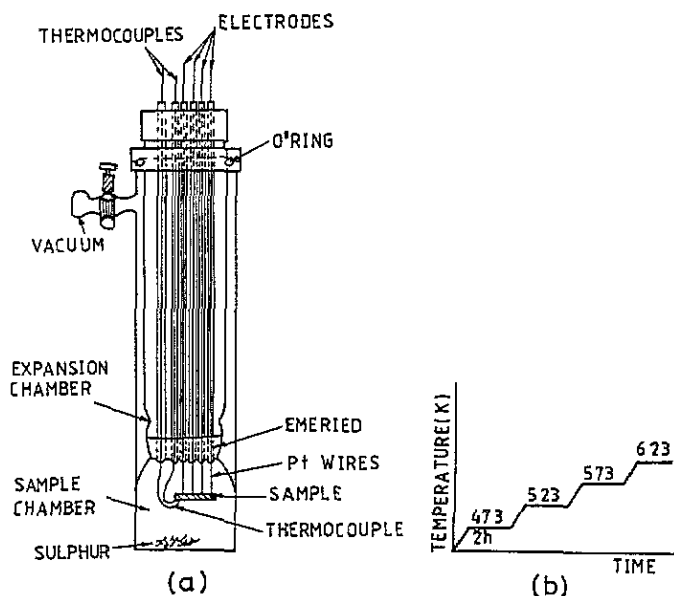


Figure 1. (a) Cell used to measure pyrite electrical resistivity in vacuum and in a sulphur atmosphere. (b) Temperature as a function of time as applied to measure electrical resistivity. Constant temperature periods are 2 h and the temperature is increased in steps of 50 K during 30 min.

consists of two glass tubes of 55 mm and 40 mm outer diameter, respectively. One tube can slide into the other allowing us to have two chambers: for sample and expansion respectively. Samples are placed as indicated in figure 1(a).

In the operation procedure once the cell has been carefully cleaned the sample is installed and the cell is evacuated up to a pressure of 10^{-3} – 10^{-4} Pa. The contacts are made with platinum wires, which are attached to the sample by four stainless steel clamps. Whenever a sulphur atmosphere is to be used, a controlled quantity (0.050 g in the present experiments) of sulphur powder is placed inside the sample chamber (of ~ 80 cm³ in volume). Sulphur vapour pressure varies between 0.26×10^3 Pa and 26×10^3 Pa in the temperature range used. Therefore the sulphur is never fully evaporated. The cell is introduced into a cylindrical furnace (85 mm diameter) so that the sample chamber is located in a controlled temperature zone and the opposite end, where the electrical connections to the measurement equipment are made, remains at room temperature.

A temperature profile such as that shown in figure 1(b) was applied to the samples with the help of an Eurotherm (model 818P4) controller-programmer. Samples rested at different constant temperatures for 2 h. The heating rate between those intervals was 2°C min^{-1} . After finishing the measurements at 723 K the samples were cooled down at a rate of 2°C min^{-1} . A Keithley (model 227) constant current source was connected to two of the cell contacts and the potential drop was measured between the other two by a Data-Precision microvoltmeter (model 2480). Both output signals from the current source and from the microvoltmeter were continuously recorded in a Yokogawa (model 3021) recorder. The sample temperature was measured with a Chromel–Alumel thermocouple placed in contact with the sample bottom. Before starting any measurement the ohmic nature of the contacts was carefully tested. The same test was also made during the measurements at different temperatures. In all cases the contacts presented the same reliable ohmic behaviour.

Natural single crystals used in this work are from the Logroño (Spain) mines. They were cut as plates of $\sim 10 \times 10 \times 1.1 \text{ mm}^3$, polished and chemically etched before the measurements. Pyrite thin films have been obtained by flash evaporation on glass substrates as described elsewhere [6] and they were $\sim 0.6 \text{ }\mu\text{m}$ thick. Fe thin films to be sulphurated in the course of the measurements were vacuum evaporated on glass substrates. Their thickness before sulphuration was $\sim 0.25 \text{ }\mu\text{m}$. Thin film surfaces were $\sim 1.5 \times 10^8 \text{ }\mu\text{m}^2$.

3. Results and discussion

3.1. Electrical resistivity of natural pyrite single crystals

The resistivity of an n-type natural pyrite single crystal at room temperature (RT) was $9.1 \times 10^{-3} \text{ }\Omega \text{ cm}$ and that at liquid nitrogen temperature (LNT) was $3.2 \times 10^{-3} \text{ }\Omega \text{ cm}$, before heating the sample. Other general characteristics were very similar to those of natural crystals of the same origin investigated some time ago [15]. The resistivity of the sample was measured in a vacuum of $\sim 10^{-4}$ – 10^{-3} Pa following the temperature profile shown in figure 1(b). Results obtained during the constant temperature intervals are depicted in figure 2(a). Once the heating was concluded the sample was cooled down to RT and a resistivity of $8.8 \times 10^{-3} \text{ }\Omega \text{ cm}$ was measured in spite of the fact that some hysteresis appeared between the heating and cooling processes. The same sample was again measured but now with sulphur powder (0.05 g) in the sample chamber in order to avoid or reduce any sulphur loss of the sample, which could lead to its decomposition. Results obtained during the constant temperature intervals are shown in figure 2(b). The sample behaviour under both atmospheres is very similar. Resistivity values ρ range between 6×10^{-3} and $3 \times 10^{-2} \text{ }\Omega \text{ cm}$ and are comparable to those obtained by several authors [1, 15–20] with other n-type single crystals. However one must note that in all cases the second run (in a sulphur atmosphere) yields smaller ρ values than the first one at the same temperature. This could be due, at least in part, to a slight perturbation (sulphur loss, oxidation, etc) suffered by the sample at the highest temperatures of the first run as has been suggested by other authors [18] and indicated by the resistivity hysteresis. However, the most striking fact from figure 2 is the ρ variation with time at constant temperature. These variations seem to obey a faster kinetics in the first run in vacuum than under sulphur atmosphere, where a stationary value of ρ is not suggested by the experimental points. On the other hand, in both groups of measurements ρ increases with time whenever the temperature is lower than $\sim 590 \text{ K}$ (open symbols in figure 2) and decreases if the annealing is carried out at higher temperatures (filled symbols in figure 2). Although we have not found any explanation for these results they could be related to reactions between defects and impurities present in high density in natural samples. In figure 3 ρ values at times $t = 0$ and $t = 120 \text{ min}$ from figure 2 have been plotted as a function of temperature. In both cases a typical behaviour corresponding to n-type pyrite is observed: ρ increases up to a maximum (extrinsic conductivity) and then decreases, indicating the beginning of the intrinsic conductivity. In this last zone different values of the thermal energy gap have been obtained by several authors (1.2 eV [17], 1.12 eV [18], 1.0 eV [21] and 0.73 eV [19]). In figure 3 two slopes corresponding to 1.2 and 0.73 eV have been drawn. It is clear that the slopes indicated by the experimental points measured in this work are in good agreement with published results.

Finally, we would like to point out that the natural sample resistivity variation with time could explain the large dispersion of reported values of the thermal energy gap: experimental results should depend greatly on the experimental procedure used by each author.

In conclusion, we can say that the device built to measure electrical resistivity up to $\sim 723 \text{ K}$ is reliable either operating under a vacuum (10^{-4} Pa) or in a sulphur atmosphere.

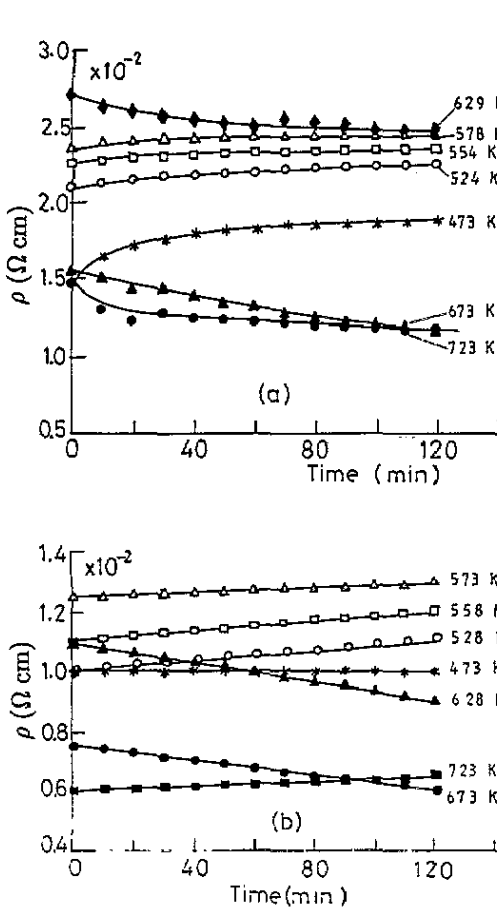


Figure 2. (a) Variation of natural single crystals' resistivity with time at constant temperature in a vacuum of 10^{-4} – 10^{-3} Pa. (b) As (a) but with the sample in an atmosphere created by 0.050 g of sulphur.

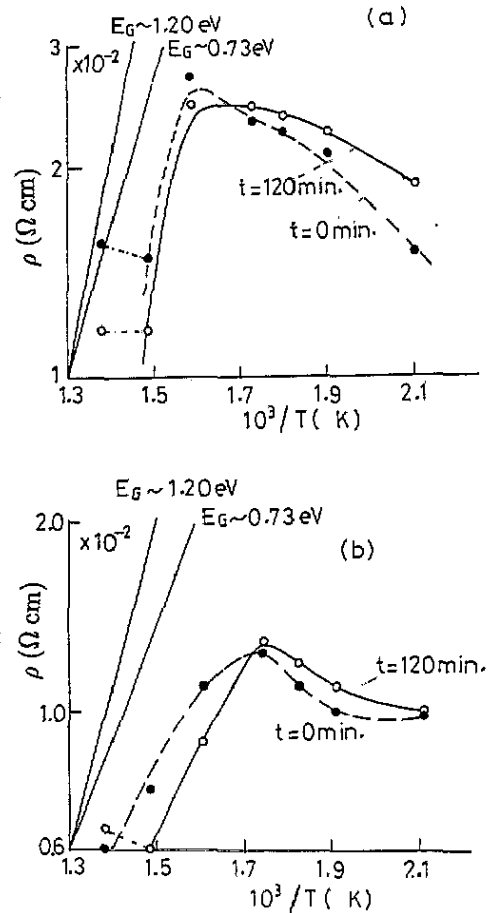


Figure 3. (a) Resistivity at $t = 0$ and $t = 120$ min (from figure 2(a)) as a function of T^{-1} . (b) As (a) with data from figure 2(b). In both figures two slopes (1.2 eV and 0.73 eV) have been drawn, corresponding to the extreme values of the thermal energy gap measured by Marinace [17] and Horita [19,20].

3.2. Electrical resistivity of pyrite thin films prepared by flash evaporation

Pyrite thin films grown by flash evaporation of pyrite powder and afterwards annealed in a sulphur atmosphere for 18 h at different temperatures have been extensively studied in our group. In particular x-ray diffraction analysis, optical absorption spectra and electrical resistivity measurements of the films at RT after the sulphuration process have been published and discussed recently [11]. However no information is available on the variation of these properties during the sulphuration/annealing process itself. Therefore the electrical resistivity of the films has been measured under a sulphur atmosphere during the same temperature profile as used with natural single crystals. The evolution of ρ with t during the constant temperature intervals is shown in figure 4(a) and the dependence of ρ on temperature at $t = 0$ and $t = 120$ min in figure 4(b). In figure 4(c) these ρ values have been plotted versus T^{-1} in order to compare the pyrite thin films with the single crystals

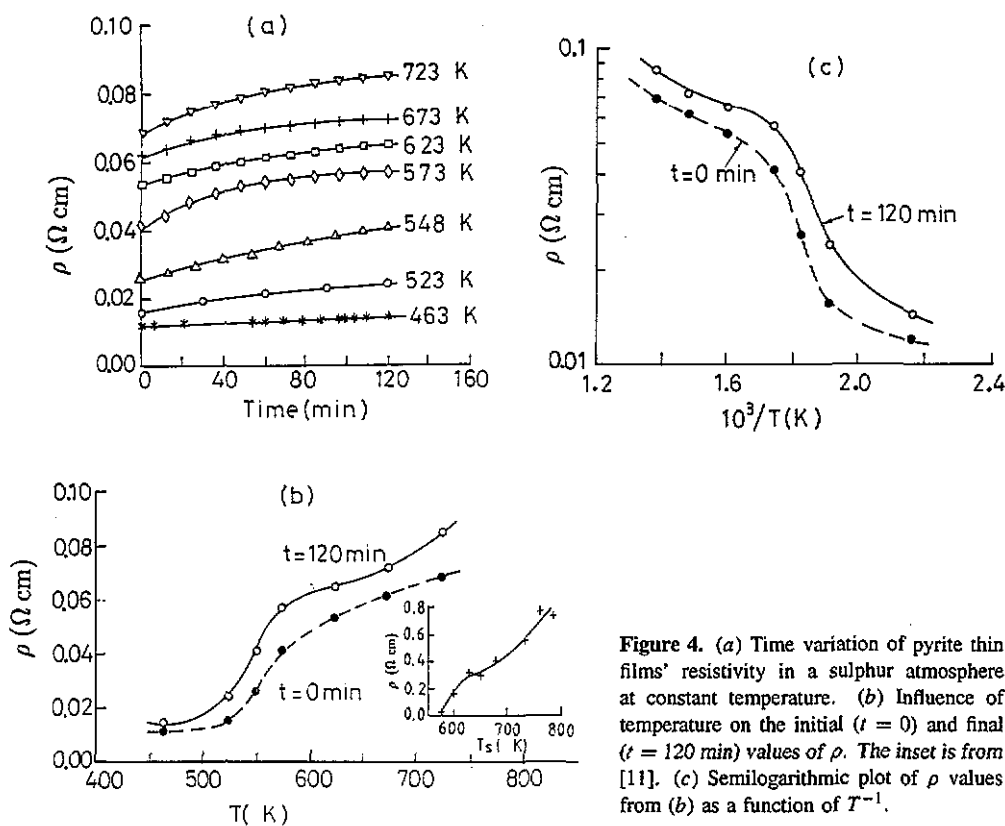


Figure 4. (a) Time variation of pyrite thin films' resistivity in a sulphur atmosphere at constant temperature. (b) Influence of temperature on the initial ($t = 0$) and final ($t = 120$ min) values of ρ . The inset is from [11]. (c) Semilogarithmic plot of ρ values from (b) as a function of T^{-1} .

(figure 3).

From figure 4(a) it is clear that ρ increases and tends to saturate with time at all temperatures. This behaviour is much clearer at higher temperatures (≥ 570 K). On the other hand, initial ($t = 0$) and final ($t = 120$ min) ρ values increase with T , showing neither the behaviour of n-pyrite nor that of p-pyrite. All these facts suggest that the pyrite films are undergoing transformations induced by annealing in the sulphur atmosphere. In fact, in a former paper [11] we have proposed that improvements in the films' stoichiometry and changes in their structure and texture are responsible for the drastic changes of the film properties. In particular, our previous results suggested that changes in the film point defect density mainly govern the behaviour of ρ at low sulphuration temperatures (≤ 600 K) and that the film crystallographic changes control the ρ variations at higher temperatures. At lower temperatures one should expect severe alterations in the number of charge carriers, and at higher ones the carrier mobility would mainly be modified. This description is supported strongly by the parallelism between the experimental points at $t = 120$ min in figure 4(b) and those measured at RT after 18 h of sulphuration at different temperatures and plotted in the inset of figure 4(b) for comparison purposes. In particular, it is worthwhile noting the change in the evolution of ρ at $T \approx 575$ – 625 K in both curves. Once again we emphasize the evolution of ρ on increasing T , i.e. on going from one open circle to the next filled one in figure 4(b): ρ remains constant or slightly increases whenever T is lower than ~ 580 – 600 K and diminishes on heating at higher temperatures. This behaviour is parallel to that shown by natural single crystals (figure 3).

The results obtained make it clear that to measure ρ variations during sulphuration itself

as a function of the process parameters is a very valuable technique, which should shed some light on the complex mechanisms operating during pyrite film sulphuration.

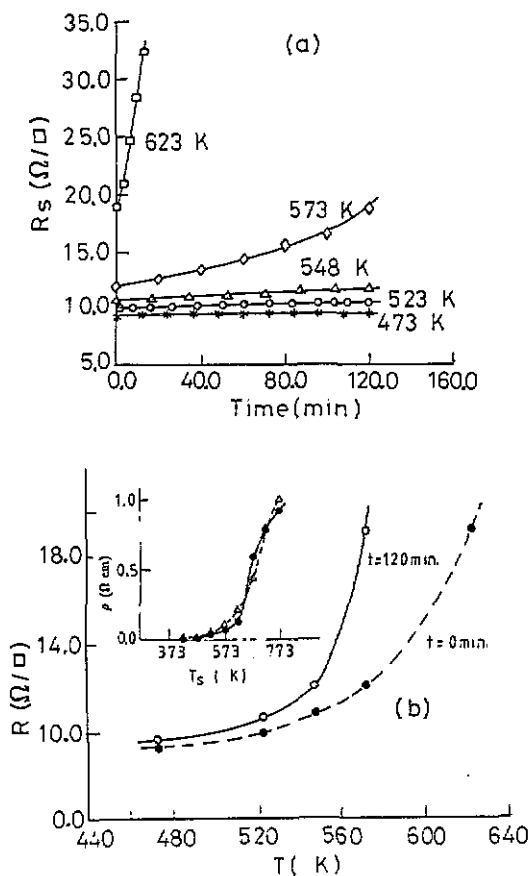


Figure 5. (a) Variation with time at constant temperature of resistivity during the sulphuration of an Fe film. (b) Initial and final values of ρ (from (a)) as a function of temperature. The small inset is from [7].

3.3. Formation of pyrite films by sulphuration of iron films

The resistivity cell has also been used to follow *in situ* the formation of pyrite by sulphuration of iron thin films. Figure 5 shows the evolution of ρ with time at constant temperature and the T influence on ρ measured at $t = 0$ and $t = 120$ min in the constant temperature intervals. The film resistance has now been expressed in ohms per square (Ω/\square) due to the film thickness variation during sulphuration. The original iron film was $0.25 \mu\text{m}$ thick and after sulphuration the pyrite film formed was twice as thick. It is clear that at temperatures around 570 K a significant alteration of the film is taking place. The influence of the sulphuration becomes more drastic between ~ 573 K and 623 K. This temperature range corresponds to that of the crystallization of pyrite films as reflected by x-ray diffraction (XRD) [7] and Mössbauer spectroscopy data [22]. Therefore, we attribute the large ρ increase to a

film transformation from the iron BCC phase to a pyrite FCC phase. At temperatures between 473 and 573 K the original iron film progressively transforms into pyrite and at ~ 623 K all the film is formed by pyrite. This behaviour is similar to that shown by some silver chalcogenides [23–25] where crystallographic transformations are accompanied by a several orders of magnitude increase of ρ .

Finally, we must note that ρ remains almost constant during the heating periods. After the whole thermal cycle the sample was cooled down to RT and its XRD pattern obtained (figure 6) confirming that a polycrystalline thin film of pyrite has been formed. Its resistivity at RT after the thermal cycle was $1 \times 10^{-2} \Omega \text{ cm}$.

These results are in good agreement with those already published [7] but obtained after long sulphuration periods (20 h). The RT resistivity of those films is shown in the inset of figure 5 for comparison purposes. In all cases it is confirmed that a new phase is formed and severe changes in the crystallization and, probably, in the point defect density of the films are produced.

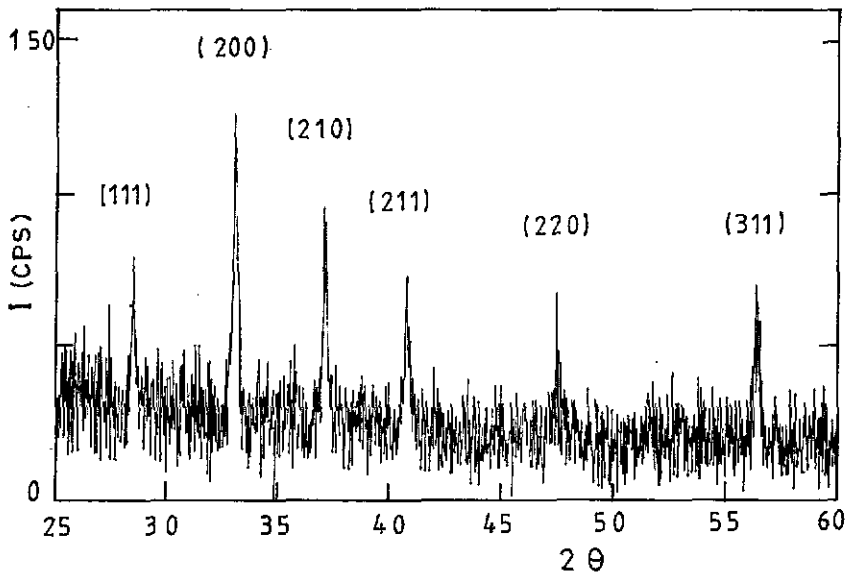


Figure 6. X-ray diffraction pattern of the sulphurated iron film (figure 5) obtained at RT.

4. Conclusions

(i) We have shown that by running a temperature profile such as that depicted in figure 1 one may study some transient phenomena (crystallization, defect kinetics) taking place in the samples during the constant temperature intervals. On the other hand, during the periods of increasing temperature one can check the extrinsic or intrinsic nature of the sample conductivity.

(ii) It has been observed that the electrical resistivity of natural single crystals changes with time: increasing in the extrinsic conductivity zone and decreasing in the intrinsic one. We have no explanation for this qualitative observation.

(iii) Changes of crystallization and stoichiometry of pyrite thin films significantly affect their electrical resistivity, which appears to be a function of time and temperature. The transformation of BCC iron into FCC pyrite is accompanied by a large increase of ρ .

Acknowledgments

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