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Abstract. Pyrite thin films have been grown by sulphuration of Fe thin films and their Seebeck coefficient has been measured as a function of the sulphuration temperature in the range 370–720 K. Films appear to be p-type (positive Seebeck coefficient) for sulphuration temperatures higher than 450 K The evolution of the coefficient with the sulphuration temperature has been qualitatively correlated with the crystallization process that the films suffer on increasing that temperature. According to our analysis, the highest value of the Seebeck coefficient obtained in our measurements ($S \approx 80\ \mu$V K^{-1}) should correspond to non-stoichiometric crystallized pyrite films formed by spheroidal grains.

1. Introduction

Pyrite thin films are obtained by sulphuration of Fe films and present different crystallization, electrical resistivity and optical properties and characteristics depending on the conditions (temperature, time, sulphur pressure...) used in the sulphuration process [1, 2]. In spite of the fact that many papers on pyrite thin films, grown by many different techniques, have been published in the last few years, it has not been possible to reach a more complete knowledge of the undoped films, mainly about their transport properties, due to the difficulties found on trying to determine the type of carrier and their Hall mobility by Hall effect measurements. This lack of knowledge is, probably, the most important barrier to progress in finding photovoltaic and/or optoelectronic applications of the pyrite thin films. Experimental results appear to be non-reproducible except for doped films [3–5]. No explanation has been proposed for this behaviour up to moment.

In order to have some information about the type of conduction of the pyrite thin films, some researchers have, sporadically, measured their Seebeck coefficient [6–8]. In all cases the sign of the obtained coefficient has been positive, indicating conduction by holes. It has been proposed that the acceptor levels are due to iron vacancies or interstitial sulphur in the pyrite lattice. The obtained values of the coefficient (ranging from $\approx$10 to 90 μV K^{-1}) are, in all cases, lower than those known from natural single crystals ($\approx$200 to $-$300 μV K^{-1}) [9–13] and also quite different from those corresponding to undoped synthetic single crystals (from $-$10 to $-$500 μV K^{-1}) [14–16]. Doped synthetic crystals have yielded a value of $\approx$22 μV K^{-1} [17].

In spite of these results, no systematic research has yet been done on the Seebeck coefficient of synthetic pyrite thin films and its relation to the preparation procedure and

structural characteristics of the films. We, in this paper, present results concerning the variation of S with the sulphuration temperature used to transform Fe thin films into pyrite films. It is shown that films prepared at low sulphuration temperatures ($T_s \leqslant 450$ K) have a very low positive or negative Seebeck coefficient. On increasing that temperature the films present higher Seebeck coefficients, which are in all cases positive. Finally, at the higher sulphuration temperatures ($T_s \geqslant 620$ K) used in this work, S remains constant or slightly increases with the sulphuration temperature. Therefore, during the transformation of the films, significant changes of the Seebeck coefficient are observed in correspondence with the evolution of the films from metallic to amorphous semiconductors and, finally, to polycrystalline semiconductors.

2. Experiment

FeS$_2$ thin films of 24 mm $\times$ 12 mm were formed on glass substrates by sulphuration of Fe thin films as described in several former papers [1–4]. The nominal sulphur pressure in all preparations was 600 Torr and the sulphuration temperature was changed from 370 to 720 K. Sulphuration time was in all cases 20 h. After sulphuration, the ampoule containing the film was open and the experimental measurements accomplished at room temperature.

The Seebeck coefficient was obtained by producing a temperature gradient between the ends of the sample of $\Delta T \sim 6$–7 K in about 10 min. Then, the heat source was regulated to reach $\Delta T = 0$ in about 15 min. Therefore, each thermal scanning yields two values of S which were in all cases in excellent agreement. Two point K-type thermocouples placed on the surface of the film measured the temperature difference, ΔT, between its ends, and two steel points, placed near the thermocouples, were able of measuring the generated thermovoltage, ΔV. The whole system was thermally isolated from the surroundings.

Both ΔT and ΔV were measured with two electrometers (Keithley, model 177). Their output signals were sent to a PC where the thermovoltage was plotted against the temperature difference. Excellent straight lines were obtained in all cases (except with samples sulphurated at $\approx$420 K which present a pronounced hysteresis as shown later on), whose slopes give the Seebeck coefficient. Whenever the films are sulphurated at $T_s \geqslant 450$ K, different measurements of the coefficient, accomplished by placing the sensors in different points of the film surface, are quite reproducible and show an experimental dispersion $\leqslant 5\%$. We have accepted the Telkes criterion [18] about the sign of Seebeck coefficient, i.e., the thermopower is taken as positive when the voltage gradient is opposite to the thermal gradient and, therefore, the hot part of the sample is electrically negative. According to this criterion the Seebeck coefficient has the same sign as the charge carriers: positive for p-type and negative for n-type samples.

3. Experimental results

The measured Seebeck coefficients are shown in figure 1 as a function of the sample sulphuration temperature. The obtained S values are, in general, of the same order of magnitude than those reported by several authors (see for example [6, 7]). The values of the Seebeck coefficient obtained with several Fe films are also shown in figure 1 as a reference. It can be seen that S changes considerably with the sulphuration temperature. At least three clear different stages can be distinguished in the curve of figure 1. At low sulphuration temperatures ($T_s \leqslant 400$ K) the obtained films show very low values of S which are quite similar to the ones corresponding to the original Fe films. This behaviour clearly
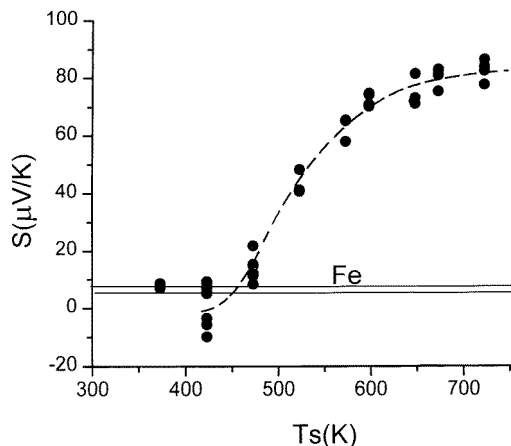
Figure 1. Variation of the Seebeck coefficient, S, of the sulphurated films with their sulphuration temperature, T_s. Two lines, as a reference, indicate the coefficient S of several Fe films. In all cases the films were sulphurated for 20 h. with a nominal sulphur pressure of 600 T. The dashed curve in the figure is an aid for the eyes.

appears in the films sulphurated at $\approx$370 K and it suggests that at this very low sulphuration temperature no substantial modification of the Fe films is produced. However, sulphuration at $\approx$420 K gives films which present positive or negative S values depending on the position of the sensors on the sample surface as indicated in figure 2. Positive S values are of the order of 5–10 μV K^{-1} as shown by the ΔV–ΔT plots of figure 2(a) and (b). They are quite similar to those of the Fe films and those of the samples sulphurated at 370 K. On the other hand, for some positions of the voltage and temperature sensors (figure 2(c) and (d)) the variation of the thermovoltage with the temperature gradient follows poor straight lines and shows a pronounced hysteresis between the thermovoltages obtained on increasing and reducing the sample temperature gradient. From the experimental points of figure 2(c) and (d), an S value can hardly be obtained. We have drawn continuous lines by fitting the experimental points by the least squares method. The slopes of these lines are quoted in the figure and are plotted in figure 1 at $T_s = 420$ K. The behaviour of the films sulphurated at this low temperature suggests that they are highly inhomogeneous and that they must be formed by different conductive and not conductive segregated phases.

On increasing the sulphuration temperature a different behaviour appears corresponding to the second stage (450 K $\leqslant T_s \leqslant$ 620 K). The coefficient S is well defined, all the films appear to be p-type and S increases with T_s. Finally, the third stage ($T_s \geqslant$ 620 K) corresponds to a region where S remains practically constant or slightly increases. By studying different groups of films sulphurated at these higher temperatures we have obtained values of S between $+50$ and $+80$ μV K^{-1}, depending on some experimental parameters (thickness of the starting Fe films, degree of doping of the sulphurated films etc). But in all cases their evolution with T_s in this third stage was similar to that shown in figure 1.

4. Discussion

The observed influence of T_s on the Seebeck coefficient can be correlated, at least qualitatively, with the formation and crystallization of the pyrite films during the sulphuration process as has been described in former papers [1, 2, 19], based on x-ray diffraction, Mossbauer effect and electrical resistivity experimental results.
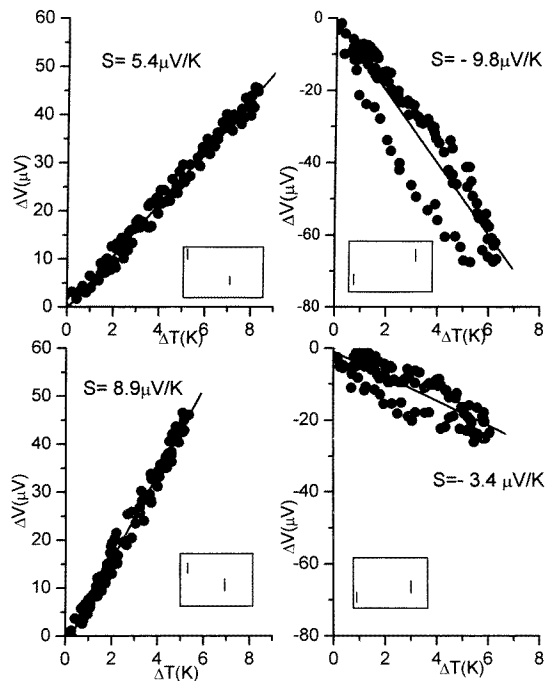
Figure 2. The thermovoltage, ΔV, against the temperature difference, ΔT, as obtained by placing the sensors in different positions on the surface of a film sulphurated at low temperature ($T_s = 420$ K). The small rectangles in the figure represent the sample surface and the vertical marks the position of the sensors.

X-ray diffraction patterns of some of the sulphurated films are shown in figure 3. The pattern of a non-sulphurated Fe film is shown in the first place. It presents a well-defined (110) peak and a weak peak corresponding to (200) planes. Films sulphurated at low temperatures (corresponding to the stage I in figure 1) give an x-ray diffraction pattern that shows either a peak corresponding to crystallized Fe or no peak at all, as expected from a film formed by amorphous or very poorly crystallized material. On the other hand, Mossbauer spectra [19] have evidenced that at very low T_s (≈ 370 K) the films are exclusively formed by Fe and no other phase was detected. In contrast, at 370 K $\leqslant T_s \leqslant$ 470 K, Mossbauer data show that the films are not homogeneous and that both pyrite and Fe are present, their proportions being variable with the film thickness. For example, films of thickness ≈ 0.2–0.3 μm that have been sulphurated at $T_s \approx 420$ K, are formed by 14% Fe and 86% FeS$_2$. Thicker films of ≈ 1 μm, grown at a sulphuration temperature of ≈ 470 K, are composed of 81% Fe and 19% FeS$_2$.

In the light of these results one could conclude that sulphurations at very low temperatures (in the range of 370 K) do not produce significant changes in the Fe film. Both the sulphur vapour pressure and the thermal activation of the sulphur molecules are very low to favour the sulphur diffusion into the Fe films. Therefore, one should expect that films sulphurated at $T_s = 370$ K give a Seebeck coefficient quite similar to that one of the non-sulphurated films, as is the case and can be seen in figure 1. On the other hand, sulphuration at slightly higher temperatures ($T_s \approx 420$ K) gives place to films which are not homogeneous and that show different Seebeck coefficients depending on the position of
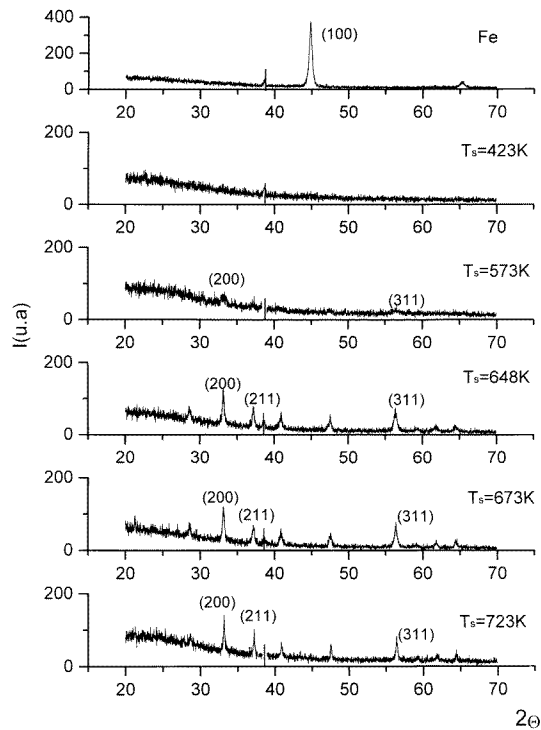
Figure 3. X-rays patterns of films sulphurated at different temperatures (indicated in the figure). The pattern of a non-sulphurated Fe film is also shown as a reference. The diagrams of samples sulphurated at other temperatures are not included for the sake of clarity. The pyrite planes corresponding to the diffraction peaks are also indicated in the figure.

the sensors on the sample surface (see figure 2). For some of these positions the voltage is negative and the experimental results show a pronounced hysteresis. This hysteresis appears to be quite reproducible with cycling. The samples have been measured on different days during a period of several months by doing ten or more cycles in each measurement. Very good reproducibility has been observed. In all the cases, the Seebeck coefficient ranged between -3.0 and -10.0 μV K^{-1}, depending on the sensor positions. The thermovoltage difference obtained between the heating and the cooling runs was $\approx$15–20 μV when the temperature difference between the hot and cold ends of the sample was $\approx$5 K. Therefore, although no clear explanation can be provided at the moment for the behaviour of the samples sulphurated at $\approx$420 K, one can say that the reproducibility of their hysteresis seems to prove that no significant change in their chemical composition is taking place during the measurements. Recrystallization of the films must be, in principle, also excluded in view of the small heating ($\approx$10 K) suffered by the samples during the measurements. Some electrical polarization induced by the thermal gradient, perhaps related to space charges in some regions of the films, could be responsible for the observed hysteresis. But this point of view must be considered a speculation for we do not have experimental evidence to support it. Samples that show the hysteresis in the Seebeck coefficient measurements reported here, has also several peculiarities in electrical resistivity and magnetoresistance. All these observations are now under investigation and a more precise report on them will be prepared in the near future.

In relation to the different signs of the Seebeck coefficient presented by the samples

sulphurated at ≈420 K (figure 2) one can say that they should be formed by, at least, two different phases: Fe and not or poorly crystallized pyrite in proportions which vary with the sulphuration temperature and thickness of the films. Although no detailed information on the distribution of both phases through the films is yet available one can speculate about the role they play on the sign of the Seebeck coefficient which changes on changing the position of the sensors on the surface films. One could think that if a continuous Fe path is connecting both thermovoltage sensors through the film, the experimental measurement should yield the Fe Seebeck coefficient or a value quite similar to it. On the other hand, the negative S values plotted in figure 1 at $T_s = 420$ K and shown in figure 2(c) and (d), should be attributed to an amorphous pyrite (or a hybrid Fe–amorphous pyrite) path between the thermovoltage sensors. This information implies that amorphous (or poorly crystallized) pyrite must have a negative Seebeck coefficient. As far as we know, no clear experimental result on the Seebeck coefficient of amorphous pyrite have been published, except those corresponding to natural samples (many of them are amorphous) which are both positive and negative [9–13].
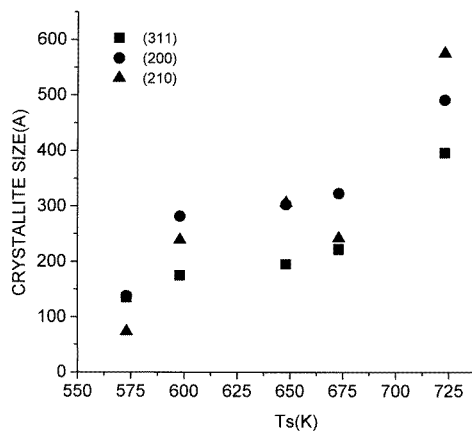

Figure 4. Variation of the pyrite crystallite size with the sulphuration temperature of the films. Values of the crystallite size are obtained by applying the Scherrer formula to the half width at half maximum of the diffraction peaks.

Crystallization of pyrite, as detected by x-ray diffraction patterns, starts at $T_s \approx 470$ K as shown in figure 3 and in [1] and [19]. The crystallization process is characterized by a continuous increase of the pyrite crystallite size on increasing the sulphuration temperature. Average values of the crystallite size have been deduced from the half width at half maximum of the x-ray diffraction peaks by applying the Scherrer formula and they are plotted as a function of the sulphuration temperature in figure 4. Crystallite sizes increase from ≈10 to ≈60 nm when the sulphuration temperature is increased from ≈470 to ≈720 K.

The Seebeck coefficient during the second stage (from $T_s \approx 450$ to ≈620 K) of the curve of figure 1 shows a continuous increase and a well defined positive sign. Films sulphurated at temperatures in this second stage are clearly polycrystalline and are formed by very small crystallites of pyrite, whose size changes from ≈10 to ≈30–40 nm on going from $T_s \cong 470$ K to $T_s \cong 620$ K, surrounded by grain or crystallite boundaries. These intercrystallite boundaries must be formed by non-crystallized pyrite or/and by a phase of segregated Fe, as suggested by the Mossbauer spectra results [19] and the Seebeck coefficient obtained at $T_s = 420$ K. Although no experimental data are available to clarify the chemical
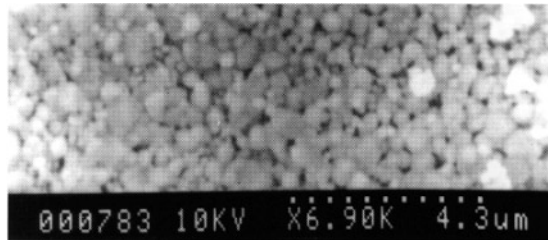
(a)
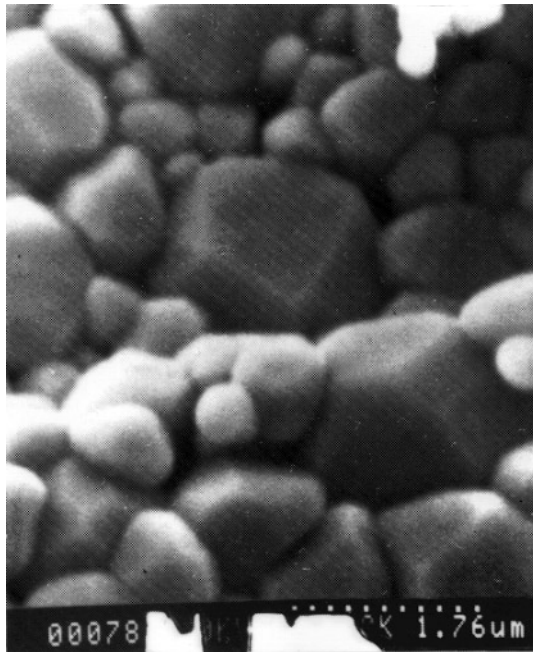
(b)

Figure 5. SEM microphotographs of films sulphurated at (a) 773 K and (b) 873 K The magnification is given at the bottom of the photographs. The films are formed by non-stoichiometric pyrite grains.

composition of the material forming the crystallite boundaries, the film Seebeck coefficient should turn out to be a combination of the value of the crystallized pyrite and that of the material forming the grain boundaries. In fact, this is the conclusion one obtains on modelling the films with a simple geometric model of cubic grains surrounded by regular plane layers of a different material [20]. Calculations based on this simple model show that S of the films changes continuously from the value corresponding to the intergrain material to that of the crystallized grain when the grain size increases and their separation is reduced. According to this view, at the higher sulphuration temperatures ($T_s \geqslant 620$ K), where the Seebeck coefficient remains practically constant, the films should be essentially formed by grains of crystallized pyrite. This appears to be the real situation as can be seen in the electron microscope photographs of figure 5 where two films sulphurated at $T_s \approx 773$ and 873 K, respectively, are presented. The film sulphurated at 773 K is formed by well defined spheroidal crystals of different sizes. No clear intergrain non-crystallized layer is seen.

This texture is much more evident on increasing T_s, as can be seen in figure 5(b), where a film sulphurated at 873 K is shown. Unfortunately, at these high sulphuration temperatures a spontaneous separation of the film from the substrate takes place and, therefore, their Seebeck coefficients cannot be measured. Experimental results of figure 1 are in agreement with this qualitative analysis if one accepts that the highest values of S obtained in our measurements ($S \approx 80 \ \mu\text{V K}^{-1}$) correspond to pure non-stoichiometric crystallized pyrite grains. This point of view is, in fact, supported by experimental measurements in synthetic films made by different authors which yield a maximum value of $S \approx 90 \ \mu\text{V K}^{-1}$ [8]. Finally, we must say that a more detailed application of geometrical models [20] to our experimental results cannot be done due to a lack of knowledge of the material forming the intergrain layers and of the evolution of their thickness with the sulphuration temperature.

Another question which must be addressed is the p-type nature of the films once their crystallization has started. Due to the purity of the starting materials (Fe and S) and to the film preparation process, we feel that the acceptor levels or acceptor states responsible for the positive sign of S should be lattice defects rather than impurity states. From this point of view one should think of Fe vacancies which act as acceptor states [21] with energy levels near the valence band, although other possibilities cannot be disregarded. In fact, it has been shown [22] that sulphur vacancies induce several energy levels in the pyrite forbidden band, one of them is very close to the valence band. Our films show a poor stoichiometry, with S/Fe values as low as 1.8 [1, 2]. Therefore, a simple energy level scheme in the forbidden band due to lattice defects is not to be expected.

In any case, we must emphasize the existing contrast between the measurements of the Seebeck coefficient, fully reproducible in values and sign, and the great difficulty found in obtaining, at the moment, reproducible values of the Hall constant at magnetic fields of 1.2 T. Further investigations seem to be necessary to clarify this point.

In conclusion, we can say that, in the light of the experimental data, the Seebeck coefficients of pyrite thin films can be correlated with their crystallization through three different stages: in the first one (370 K $\leqslant T_s \leqslant$ 450 K) very low values of S are measured and their sign is that corresponding to Fe or is not clearly defined due to the two phases (Fe and non-crystallized pyrite) that compose the film. In the second one (450 K $\leqslant T_s \leqslant$ 620 K) S acquires higher values and a clear positive sign due to the crystallization of the film and to the continuous increase of the size of the pyrite grains. Finally, the third stage ($T_s \geqslant$ 620 K) is characterized by a practically constant value of S reflecting the fact that the films are formed by pyrite grains and no significant role is played by the intergrain material.

Acknowledgments

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