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Preparation of pyrite films by plasma-assisted sulfurization of thin iron films

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Pyrite films were prepared using the pure elements as source materials: thin iron films were evaporated on quartz substrates and exposed to a sulfur plasma. The process was controlled by a transmission measurement. X-ray spectroscopy was used to characterize the films and preliminary optical and electrical measurements were carried out.

Thin pyrite films have become of certain interest for solar cell applications in the last few years. Due to the band gap of 0.95 eV and the large absorption coefficient of $\alpha = 6.4\times10^5$ cm^{-1} (Ref. 1) pyrite films became a candidate for thin-film solar cells. The solar energy conversion efficiencies of the cells prepared so far are, however, restricted to approximately 3%, which is probably due to defects, impurities, nonstoichiometry, and the unknown chemistry of the interface of pyrite films.

Up to now thin films were prepared by thermal evaporation of natural *n*- or *p*-type pyrite,[2-4] metalorganic chemical vapor deposition of ironpentacarbonyl and sulfur or H_2S,[5] spray pyrolysis of $FeCl_3$, thiourea and sulfur,[6,7] and by the reaction of ironpentacarbonyl with a sulfur source (S or H_2S) in an organic solvent.[8] In this letter we report on an alternative method for the preparation of FeS_2 films, using a rf plasma and the pure elements iron and sulfur as source materials. First results of a structural, electrical, and optical characterization of these pyrite films are presented.

The pyrite films were prepared in a two-step process. Thin iron films were evaporated on quartz substrates, which were then exposed to a sulfur plasma for sulfurization. The quartz substrates of $20\times10\times1$ mm^3 in size were cleaned in chromic acid for 10 min, rinsed with de-ionized water at least five times, and heated for 2 h at 200 °C to eliminate water from the surface. This cleaning procedure seemed to be more suitable to get homogeneous films than cleaning with organic solvents. The iron films of about 400 Å thickness were evaporated by electron beam evaporation. The iron source was five times zone refined and showed the following contamination levels: $C<8$ ppm, $N<1$ ppm, $H<0.1$ ppm, $O<10$ ppm, $S<10$ ppm. The thickness of the films and the evaporation rate of about 10 Å/s were monitored by a quartz crystal. The residual gas pressure in the vacuum chamber was about 8×10^{-6} mbar. After evaporation the films were kept under argon atmosphere in a desiccator to prevent oxidation or contamination until they were treated with the sulfur plasma.

Our system for the sulfur reaction was optimized several times, leading to the system shown in Fig. 1. The reaction chamber was a quartz tube of 2 cm diameter and T shape with sulfur (J. Matthey 99.999%) in the arm showing downward and the iron film in the horizontal tube. In a previous arrangement where the sulfur and the iron film were positioned next to each other, the films often showed nonhomogeneity because small sulfur particles contaminated the film surface during loading or evacuating the system. With the above arrangement it was further possible to control the temperature of the sulfur and the film separately. The film was positioned outside the plasma reactor. Thus a resistance heater with thermocouple and a transmission measurement tool could easily be applied. As the transmission for photon energies below 1 eV increases (i.e., iron transforms to pyrite), it was thus possible to monitor the degree of reaction during the process. The measurement setup was adjusted to the problem using a halogen lamp, a Ge diode detector, and a silicon filter. Although the iron film was not inside the rf generator, the film was positioned in the active luminous range of the plasma, due to the influence of the metallic heater on the plasma. The generator worked at 13.6 MHz with 60 W power. The reaction chamber could be evacuated by a diffusion pump. To protect the diffusion pump from contamination with sulfur, a cooling trap, filled with liquid nitrogen, was mounted between the pumping system and the reactor. Before the reaction was started the chamber was always evacuated and filled with argon gas several times.

Figure 2 shows the transmission of the growing pyrite layer during the reaction. First the sulfur was heated in order to melt and a pressure of 2×10^{-2} mbar established. Then the temperature of the film was increased and the yellow color, which is typical for pyrite, appeared. At about 250 °C, depending on the heating parameters, the transmission decreases rapidly and then starts to increase as would be expected. The initial decrease may be due to diffuse reflection, a reaction with a thin oxide layer or the formation of a metallic FeS layer, but this needs further investigation. However, it was found that the film is sputtered off when the plasma process was started before this transmission drop appeared. Therefore we started the plasma treatment after this anomaly. When the transmission saturated, the rf generator and the film heater were

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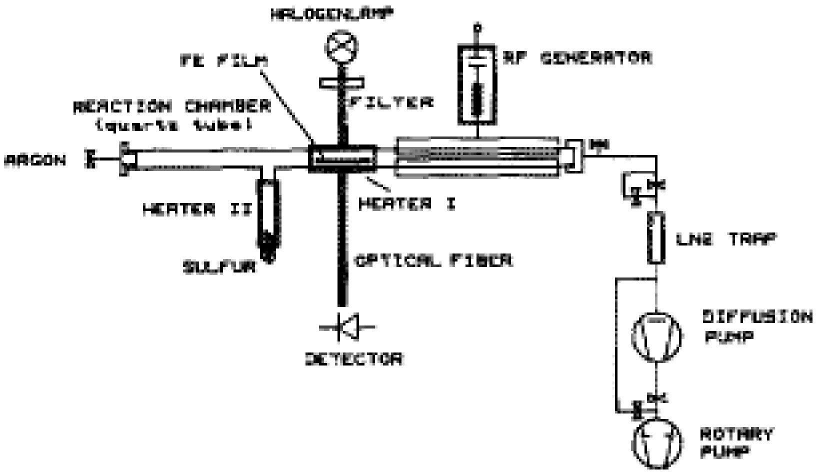

FIG. 1. Schematic view of the system for the sulfurization of iron films.

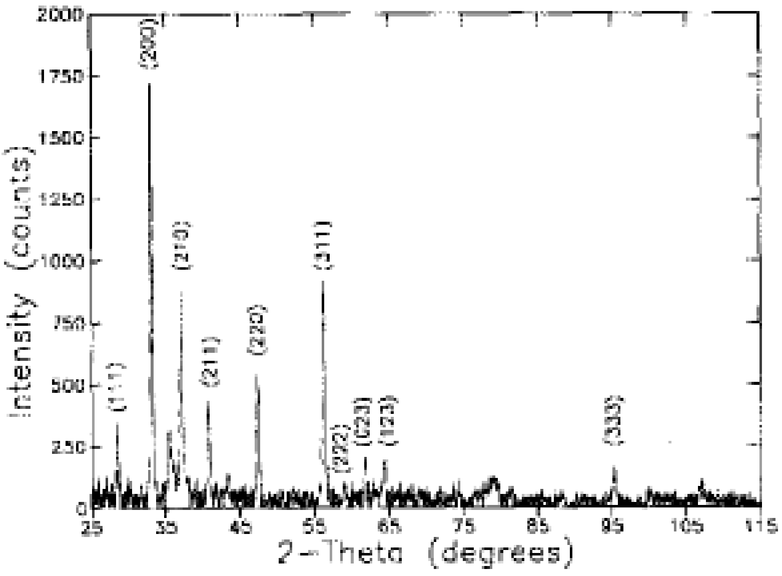

FIG. 3. Diffraction pattern with marked pyrite hkl reflections (Ref.: ASTM 24-76A) of a 400-Å-thick iron film after being treated for 12 min in a sulfur plasma at 441 °C. The sulfur gas pressure was 7×10^{-2} mbar. The peaks marked with * belong to a Fe_2O_3 phase.

switched off and a second increase in transmission was found, probably due to the decreasing film temperature. The films were characterized by a Siemens D501 diffractometer. The typical diffraction pattern for pyrite was found when the temperature of the iron film was higher than 200 °C (Fig. 3).

We calculated the grain size of the films by Scherrer's equation from the x-ray line broadening.[5] The values for films being treated at about 400 °C varied between 350 and 800 Å. The grains seem to be randomly distributed as the ratio of the peak heights is approximately the same as for a powder diffraction pattern. The temperature dependence of the electrical conductivity is shown in Fig. 4. For the temperature range above 170 K the plot can be approximately described by a function $e^{-E/kT}$ with $E=209$ meV and below 170 K with $E=88$ meV. Thermoprobe measurements indicated a *p*-type semiconductor. Figure 5 shows the spectral absorption for the same film. In order to investigate the influence of the plasma and the external heating on the sulfurization process, we prepared films without external heating or by a pure thermal reaction.

Iron films of 800 Å thickness, which were treated for 15 h in the sulfur plasma without heating, showed only a thin layer of pyrite at the surface. This layer probably acts as a diffusion barrier for sulfur and prevents the bulk from further sulfurization. The pure thermal reactions were carried out in quartz tubes. They were etched, filled with an iron film at one end and sulfur at the other, evacuated, and then sealed. Then the reaction tubes were heated for 18 h at a constant temperature and afterwards cooled down slowly. The end with the sulfur had to be cooled down faster than the end with the pyrite film in order to avoid condensation of sulfur gas on the film. A film heated to 670 °C showed also the typical diffraction pattern of pyrite and no other phases. Thus the plasma assistance is not necessary for the sulfurization of the iron films but it supports the process decisively.

It is possible to prepare thin pyrite films by a plasma-assisted thermal reaction of iron films with sulfur gas at temperatures below 450 °C. Further work will have to be carried out for an improved understanding of the preparation process and the electrical and optical properties of the films which might eventually be suitable for solar cell applications.

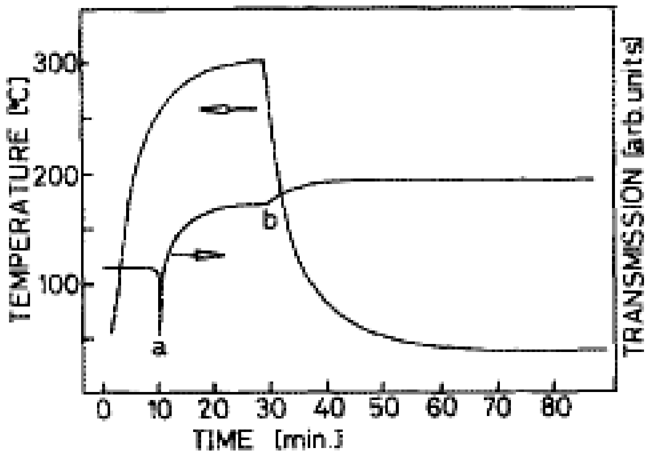

FIG. 2. Typical result for the measurement of temperature and transmission during sulfurization. *a* and *b* indicate the beginning and the end of the plasma process.

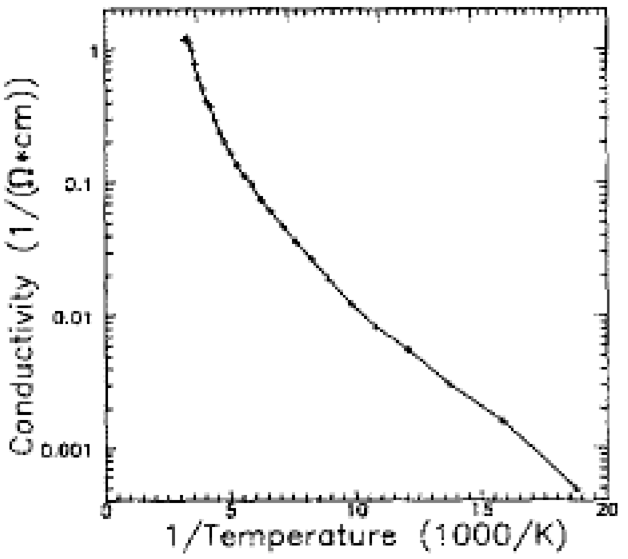

FIG. 4. Temperature dependence of the conductivity for a sample which was plasma treated for 12 min at 439 K.

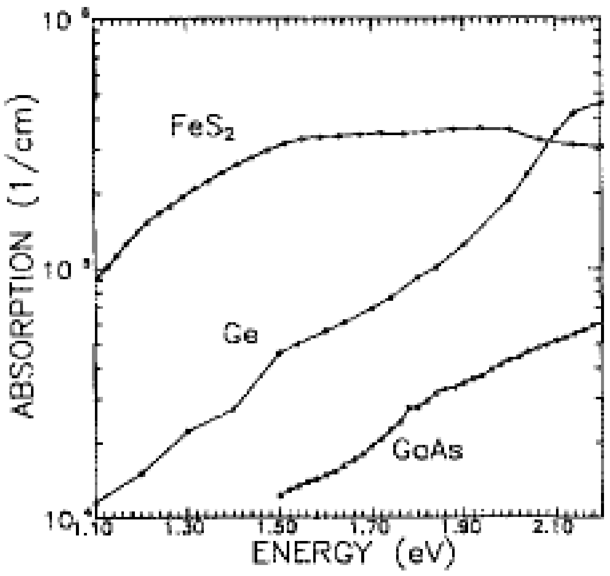

FIG. 5. Spectral absorption of a typical pyrite film compared to the absorption of germanium and gallium arsenide.

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