

Observation of the Structure of Iridescent Surface Layer on Chalcopyrite

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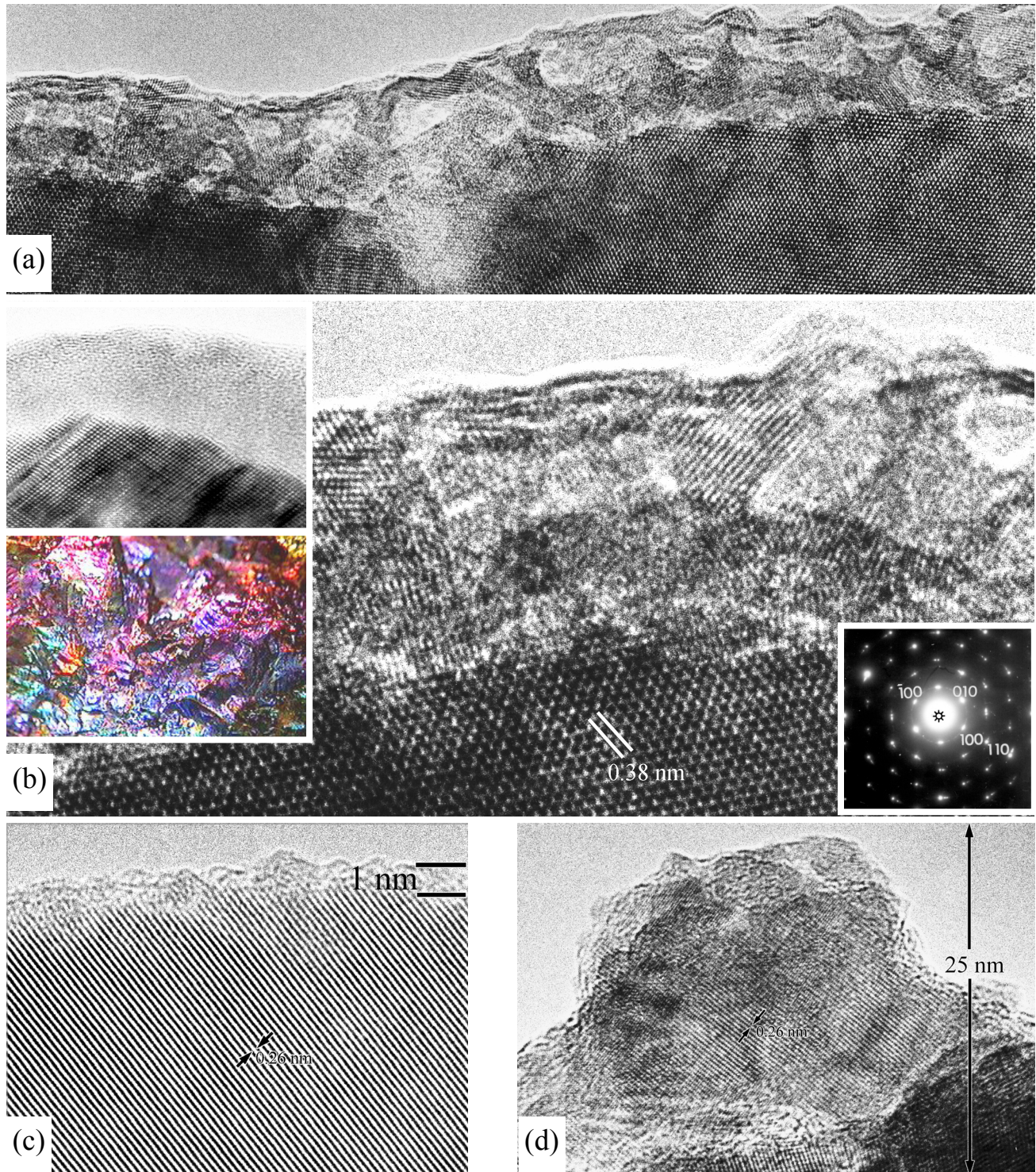
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Chalcopyrite (CuFeS_2) is a well-known mineral with space group I-42d and lattice constants $a=0.528\text{nm}$ and $c=1.04\text{nm}$. It has a double sphalerite or ZnS structure. In a TEM study, it was shown that chalcopyrite develops magnetic (110) domains originating from a reversible magneto-elastic deformation [1]. The iridescence on sulphide minerals originates from oxidation, which occurs on chalcopyrite, pyrite and pyrrhotite [2-3]. Pyrite and chalcopyrite initially transform into ferrous or cuprous thiosulfates, which further oxidize into ferric and cupric sulfates. Elemental Sulfur is also a byproduct of these oxidations. The iridescence on chalcopyrite is characteristically colourful, exhibiting various colours, inset Figure 1b. The iridescence seen is similar to that on a thin layer of oil on water, where light reflects off the top and back surface on the film, which is only few wavelengths in thickness. Constructive interference occurs when the path difference is an integer number of the wavelengths, whereas for an integer plus a half, destructive interference takes place. In this contribution, we report the results of the high-resolution TEM (HRTEM) studies on the structural and microstructural characteristics of an iridescent surface layer that had developed on chalcopyrite as a consequence decomposition by exposure to the atmosphere.

Several surfaces of the mineral chalcopyrite CuFeS_2 , which had become tarnished and iridescent, were studied by high-resolution TEM. The iridescent surfaces imaged on crushed specimens, varied in thickness and morphology, were often amorphous but occasionally contained different amounts of isolated crystalline inclusions, Figures 1a-d. The interfaces between the iridescent layers and the actual crystals in the interior on which iridescence had occurred, were either chalcopyrite or occasionally, pyrite, FeS_2 . These interfaces were often sharp but also contained evidence of corrosion-related interpenetrating planar defects, inset Figure 1b. Small amounts of Fe_2O_3 in polycrystalline form were identified by simulations methods, but the presence of numerous other observed phases in nanometer scale indicated the complexity of surface decomposition and possible alterations of chalcopyrite into the mineral Bornite (Cu_5FeS_4), or Covalite (CuS) or combinations of a variety of non-stoichiometric structures. Decomposition into elemental sulfur, Fe or their oxides is a possibility, but they could not be identified by simulations or x-ray microanalysis. In certain regions, crystalline inclusions were absent and a continuous amorphous layer had formed, inset Figure 1b. The thickness of the surface layers varied significantly, ranging from 1nm to about 50nm. Crushed samples studied using HRTEM proved successful in identification of certain microstructural characteristics of the iridescent layers. Ion milling would have been unsuitable to this study.

References

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Figures 1a-d. HRTEM images illustrating a variety of structural and microstructural nature of surface decomposition on chalcopyrite. a) Nano-size crystalline and amorphous islands coexist. b) Crystalline islands show varied texture and the interface is undulating. Insets: (top) planar defects rarely observed are pinned to the amorphous surface layer, (bottom): the colourful appearance of chalcopyrite. c) Thin amorphous layer at specimen edge and d) Pile up of surface decomposition.