X-RAY AND ELECTRON DAMAGE, AND PHOTOCHEMICAL REACTIONS IN CdS SINGLE CRYSTALS AND LAYERS, AND ANNEALING OF THESE DEFECTS

FINAL REPORT
July 1967

Contract No. NsG-573
National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

by

K. W. Böer
Principal Investigator
Physics Department
University of Delaware
Newark, Delaware

The work done within the period of the grant has been reported in fifteen technical reports, eight of which have been published. The main results shall be summarized in this final report.

It has been shown that marked changes in the spectral distribution of the photoconductivity of CdS and in the thermally stimulated current (TSC)-curves occur at x-ray irradiation slightly above 250 keV, provided the CdS crystals are kept in ultrahigh vacuum ($p \lesssim 3 \times 10^{-10}$ torr) at room temperature (1)*. Earlier observations of changes of photoelectric properties after x-ray irradiation at or below 100 keV are caused by surface effects in vacua of 10^{-5} to 10^{-6} torr. Therefore more intensive studies of the influence of gas adsorption and desorption from the CdS surface in ultrahigh vacua (10^{-10} torr range) have been carried out (5, 11) and have proven that especially ionized oxygen can change markedly the photoconductance at vacua as low as 10^{-10} torr. Desorption of oxygen (as observed by mass-spectrometer-analysis) takes place in several desorption steps (at different temperatures) indicating multi-layer or multi-site oxygen adsorption (11).

X-ray irradiation at 300 keV produces defects, which, in the most economical model can be described as sulfur vacancies close to the crystal surface (4, 14) due to focussing collisions. These defects cause the increase of a glow maximum at 350°K (1, 4, 14). Also an increase of the density of recombination centers is observed, which continues to grow at the expense of the density of sulfur vacancies after x-ray damage has stopped. It

---

* The numbers in parenthesis refer to the number of the technical report.

is assumed that these recombination centers are defect associates, containing a sulfur vacancy and an unknown partner (14). The production of these associates is stopped at liquid N_2 - temperatures.

Heat treatment of CdS in sulfur vapor decreases the x-ray damage-effect drastically, and is described due to a decreased probability to produce sulfur vacancies close to the surface (13). Vacuum treatment reversed the effect of a previous sulfur treatment (13, 14).

More extensive investigations of the change in defect-structure due to sulfur-treatment (12, 15) and to vacuum heat treatment (2, 9, 10) were carried out. It was observed that a heat treatment in a sulfur atmosphere between 500 and 700°C predominately reduced the density of doubly ionized sulfur vacancies up to about 520°C, changes the density of single ionized Frenkel defects between 520 and 620°C and reduces the density of doubly ionized Cd-interstitials above 620°C (15). Vacuum treatment at 150° to 350°C at about 10^{-9} torr results in dissociation of higher defect associates (2), and production of single defects which can be frozen-in at room temperature. It is proposed for explanation of the experimental results that cadmium vacancies are produced, which cause a glow peak at 200°K (9, 10). The cadmium double-vacancy is identified with a glow peak at 440°K (10).

X-ray produced defects anneal out at about 100°C (14). For electrical measurements at elevated temperatures it was necessary to have ohmic contacts which withstand heat treatments better than In- or Ga- electrodes. Ti-Al sandwich electrodes were developed which do not change their ohmic properties at heat treatments up to 300°C (3, 6).

Finally recrystallization of CdS evaporated layers

was investigated in order to learn more about the defect structure of CdS (7, 8). It was observed that some intrinsic defects, presumably sulfur vacancies can be annealed-out by stress enhanced recrystallization to an unusually large degree leaving less than 10^{11} cm^{-3} traps at about 0.6eV below the conduction band (7) and resulting in very sensitive and unusually fast photo-response (8).

The work is being continued with support from other sources.

TECHNICAL REPORT LIST

1. K. W. Böer, J. C. O'Connell, R. Schubert — X-Ray Damage and Annealing of These Defects in CdS Single Crystals, Lum. Symposium Verl. K. Thiemig KG, Munich (1966) p.223.

2. K. W. Böer, C. A. Kennedy, J. C. O'Connell — Production And Annealing of X-Ray and Thermal Damage in CdS Single Crystals, (N.Y.C.), Bull Am. Phys. Soc. II, 17 (1966)

3. R. B. Hall — Electrical Contacts to CdS Single Crystals, (Masterthesis)

4. K. W. Böer, J. C. O'Connell — Intrinsic Point Defects in CdS Proc. International Conf. on Luminescence, Budapest (1966)

5. K. W. Böer, R. Schubert — Influence of Oxygen in the Ultra-High Vacuum Range on the Electrical Properties of CdS, phys. stat. sol. 16, K5 (1966)

6. K. W. Böer, R. B. Hall — Multilayer Ohmic Contacts on CdS, J. Appl. Phys. 37, 4739 (1966)

7. K. W. Böer, J. W. Feitknecht, D. G. Kannenberg — Properties of Recrystallized Evaporated CdS Layers, phys. stat. sol. 16, (1966)

8. K. W. Böer, A. S. Esbitt — Evaporated and Recrystallized CdS Layers, J. Appl. Phys. 37, 2664 (1966)

9. C. A. Kennedy — Intrinsic Defects in CdS, (Masterthesis)

10. K. W. Böer, C. A. Kennedy — Vacuum Heat Treatment of CdS Single Crystals, phys. stat. sol. 19, 203 (1967)

11. R. Schubert — Gas Desorption from Virginal CdS Crystals, phys. stat. sol. 16, K157 (1966)

12. K. W. Böer, W. J. Nalesnik — Change of Electrical Conductivity of CdS Single Crystals During Heat Treatments in Sulfur Vapor Between 500° and 700°C. Bull. Am. Phys. Soc. 12, pp. 120 (1967)

13. K. W. Böer, J. C. O'Connell — Production & Annealing of Intrinsic Defects in X-Ray Irradiated CdS Single Crystals, Bull Am. Phys. Soc. 12, pp. 347 (1967)

14. J. C. O'Connell — Production & Annealing of Intrinsic Defects in X-Ray Irradiated Cadmium Sulfide, (PhD. Thesis)

15. W. J. Nalesnik — Change of Electrical Conductance of CdS Single Crystals During Heat Treatments in Sulfur Vapor Between 500° and 700°C, (Masterthesis)