ISSN 1330–0008
CODEN FIZAE4

SOME STUDIES ON CHEMICALLY AND THERMALLY PREPARED $CuInS_2$ FILMS

SIHAM MAHMOUD and ABDEL-HAMID EID

Electron Microscope and Thin Film Department, National Research Centre, Cairo, Egypt

Received 7 July 1997

UDC 538.975

PACS numbers: 73.61.Jc, 78.66.–w

Copper indium disulfide ($CuInS_2$) thin films were thermally and chemically prepared, and the structural, optical and electrical properties were investigated. X-ray analysis indicates only single-phase chalcopyrite with no extra planes. The optical and the thermal energy gap was determined. The gap of the annealed thermally-prepared samples in sulfur vapour is greater than of the as-deposited films, which indicates the decrease of d-level contribution to the valence band.

1. Introduction

The ternary compound $CuInS_2$ belongs to the I-III-VI family of semiconductors with chalcopyrite type structure [1]. Its space group is I42d, with tetragonal unit cell in which the copper and indium atoms sit in distinct lattice sites. In recent years, this group of materials has received considerable attention due to their oriented use in many opto-electronic applications in efficient thin-film solar cells [2,3]. The electrical conductivity of the n-type $CuInS_2$ is governed by sulfur vacancies, copper vacancies and indium interstitials, while the p-type is characterized by interaction of sulfur and copper vacancies [4]. B. Tell et al. [5] have found that all the copper compounds are readily made p-type by annealing at a temperature in the range 873 to 1073 K in sulfur vapours. The fundamental energy gap has been studied by many investigators [5–8]. Its direct value lies in the range between 1.50 and 1.55 eV at room temperature, and slightly increases at lower temperatures [9]. The temperature dependence of the energy gaps for sulfur annealed $CuInS_2$ films has been studied by photo-reflectance method in the temperature range of 10 to 300 K. The reported values indicate considerable discrepancies [10]. The present work is dealing with the structure and temperature dependence of the optical and thermal energy gap of $CuInS_2$ films prepared by different techniques.

2. Experimental techniques

Thin $CuInS_2$ films 100 to 400 nm thick were prepared by the thermal evaporation under high vacuum and by the chemical bath deposition (CBD) from copper, indium and sulfur complexes. For the evaporation method, the starting ingot was prepared by mixing stoichiometrically elements of copper, indium and sulfur in a sealed silica tube which was then evacuated to a pressure of about 10^{-2} Pa. The mixture was then heated at 873 K for 55 hours. The films were thermally deposited by evaporation from a tungsten boat, under a vacuum of 10^{-4} Pa. The deposition was carried out on pre-cleaned glass slides which were kept at room temperature during the film deposition.

The chemical bath deposition is based on the slow reaction between the slowly released Cu^+, In^+ and S^- ions from their complexes according to the following steps:

$$CuCl_2 + NH_3 \rightarrow [Cu(NH_3)_4]^{2+} \tag{1}$$

$$InCl_3 + TEA \rightarrow [In(TEA)]^{2+} \tag{2}$$

$$CS(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^- \tag{3}$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \tag{4}$$

The overall reaction is:

$$[Cu(NH_3)_4]^{2+} + [In(TEA)]^{2+} + S^{2-} \rightarrow CuInS_2 + \text{solution}, \tag{5}$$

where TEA is the triethanolamine solution ($C_6H_{15}N$).

The temperature of the growth solution was maintained at about 338 K during the deposition. The film thickness was measured by the interference and by weighing methods. The optical properties of the films were determined from the transmission spectra obtained by Shimadzu-240 spectrophotometer over the spectral range 300 to 900 nm. The structural analyses were carried out using JOEL Model JSM-T20 scanning electron microscope and Philips PW 1390 X-ray diffractometer. The resistance was measured directly using Keithley 617 programmable electrometer having an input impedance of about 10^{16} Ω.

3. Results and discussion

The surface topography of $CuInS_2$ films prepared by chemical bath deposition method was studied by the scanning electron microscope. The surface of the deposited layers is smooth and well adherent to the substrate. A homogeneous film was observed over large areas. The grain size increases and better grain boundaries appeared when increasing the film thickness (Figs. 1a, b and c). The grain size increases and becomes uniformly distributed over the whole area when heating the films at 523 K in vacuum. Some aggregates of opaque grains can be observed as shown in Fig. 1d. This behaviour is compared with the data of X-ray diffraction shown in Fig. 2. Weak diffraction peak was recorded for the as-deposited film. By heating the film at 523 K, the presence of reflection planes (112) strongly imply the formation of the chalcopyrite phase. Also, these results indicate that the crystallinity of the film has been improved by the annealing treatment, in accordance with the work of Samaan et al. [11].

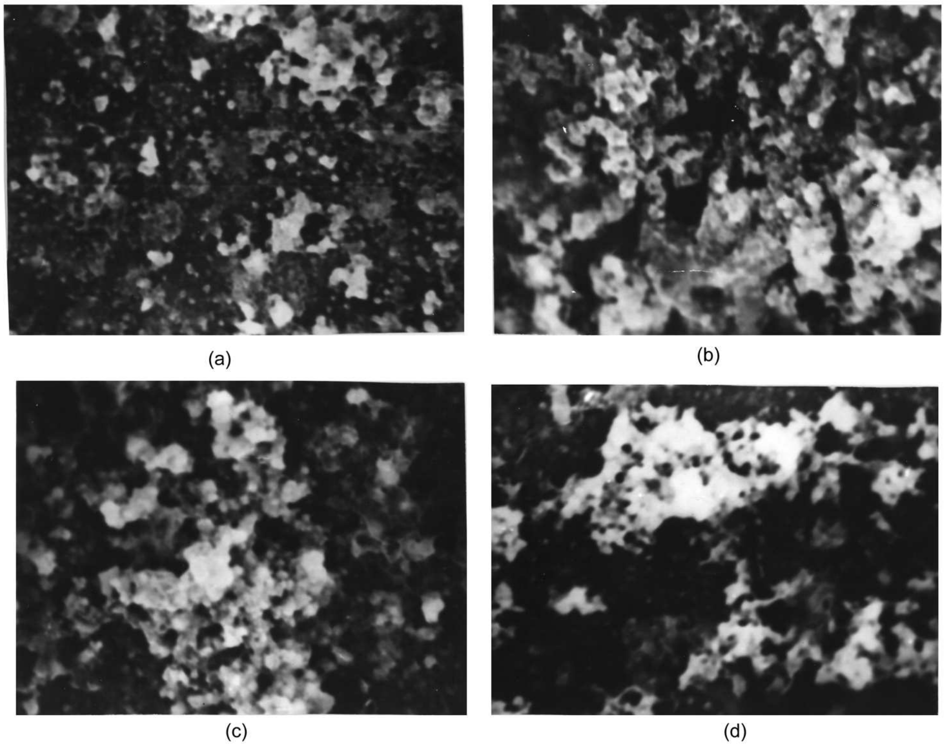

Fig. 1. Scanning electron micrographs of chemically deposited $CuInS_2$ *films of thickness a)* $d = 150$ nm, *b)* $d = 200$ nm, *c)* $d = 230$ nm *and d)* $d = 230$ nm *heated at 523* K.

The absorption coefficients α of the films were estimated from the normal incidence transmittance T and the corresponding calculated phase shift θ_f for limited wavelength regions, according to the relations [12]:

$$T = \frac{T_f n_s T_s}{1 - R_b(1 - T_s)}, \tag{6}$$

$$n_s T_f = \frac{16 n_s (n^2 + k^2)}{C^2 + D^2}, \tag{7}$$

$$\theta_f = \arctan \frac{kC + nD}{kD - nC}, \tag{8}$$

where

$$T_s = \frac{4n_s}{(1+n_s)^2}, \tag{9}$$

$$\begin{aligned} C = \; & e^K\{[(1+n)(n+n_s)-k^2]\cos N + k(1+2n+n_s)\sin N\} + \\ & e^{-K}\{[(1-n)(n-n_s)+k^2]\cos N - k(1-2n+n_s)\sin N\}, \end{aligned} \tag{10}$$

$$\begin{aligned} D = \; & e^K\{[(1+n)(n+n_s)-k^2]\sin N - k(1+2n+n_s)\cos N\} - \\ & e^{-K}\{[(1-n)(n-n_s)+k^2]\sin N + k(1-2n+n_s)\cos N\}, \end{aligned} \tag{11}$$

where

$$K = 2\pi kd/\lambda, \qquad N = 2\pi nd/\lambda, \quad \text{and} \tag{12}$$

$$\alpha = 4\pi k/\lambda. \tag{13}$$

Here, n and k are the optical constants of the film, T_f is the transmitted amplitude inside the substrate, T_s is the transmittance of the substrate surface, R_b is the reflectance from the back of the film inside the substrate and n_s is the refractive index of the substrate.

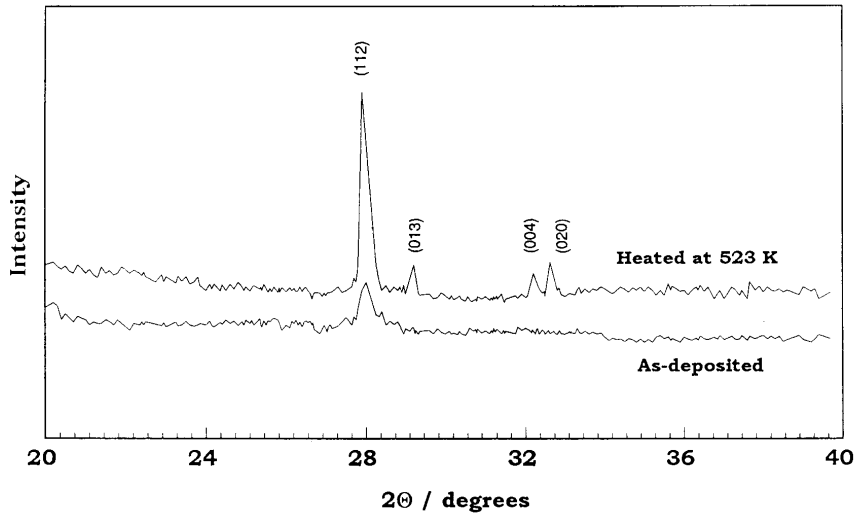

Fig. 2. X-ray diffraction of chemically deposited $CuInS_2$ *films.*

Figures 3a and 4a show the transmittance T versus the photon wavelength λ for the as-deposited and for the annealed, chemically and thermally prepared $CuInS_2$ films nearly 230 nm thick. The curves demonstrate high transmittance beyond the edge, which indicates that the prepared films are of minimum impurity and lattice defects.

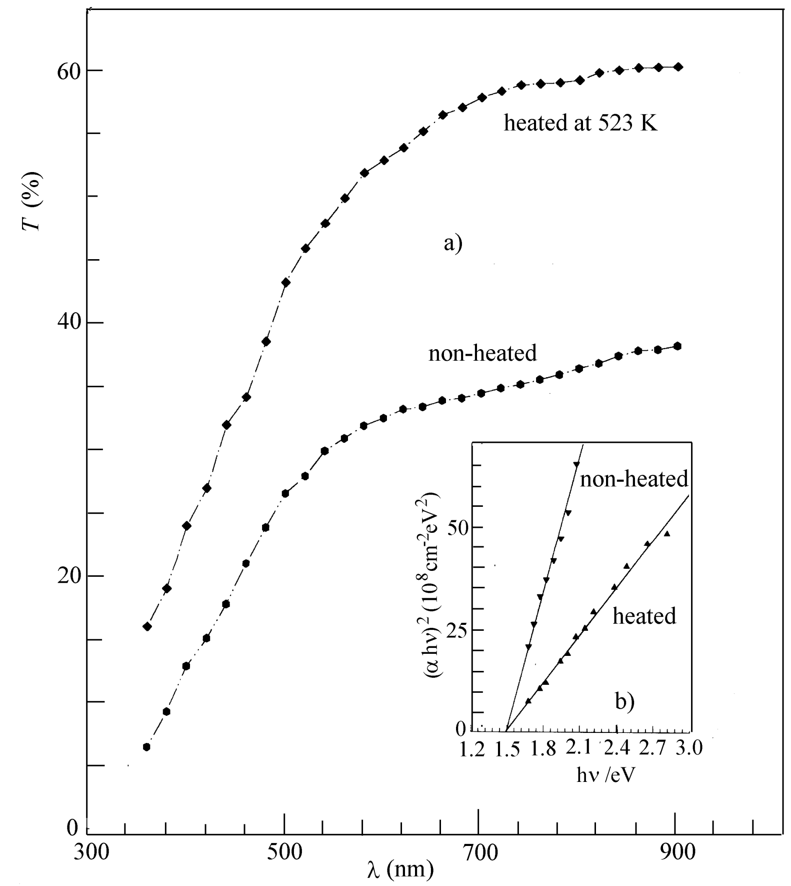

Fig. 3. Plots of a) T vs. λ, b) $(\alpha h\nu)^2$ vs. $h\nu$ for chemically deposited $CuInS_2$ *films.*

The absorption data around the gap edge were analysed using the direct transition relation of the form:

$$\alpha h\nu \sim (h\nu - E_g)^{1/2}. \tag{14}$$

The allowed energy gap E_g was determined from the extrapolation of the linear part of plot of $(\alpha h\nu)^2$ vs. $h\nu$ as shown in Figs. 3b, 4b and 4c. This is expected since $CuInS_2$ is a direct band-gap semiconductor [3]. The plots show that energy gap of the chemically as-deposited and annealed films is 1.5 eV (Fig. 3b). This value is higher than the value of 1.45 eV reported by Bihri et al. [13] and in good accordance with the value of 1.5 eV reported by Binsma et al. [14,15] and Padam $CuInS_2$ films.

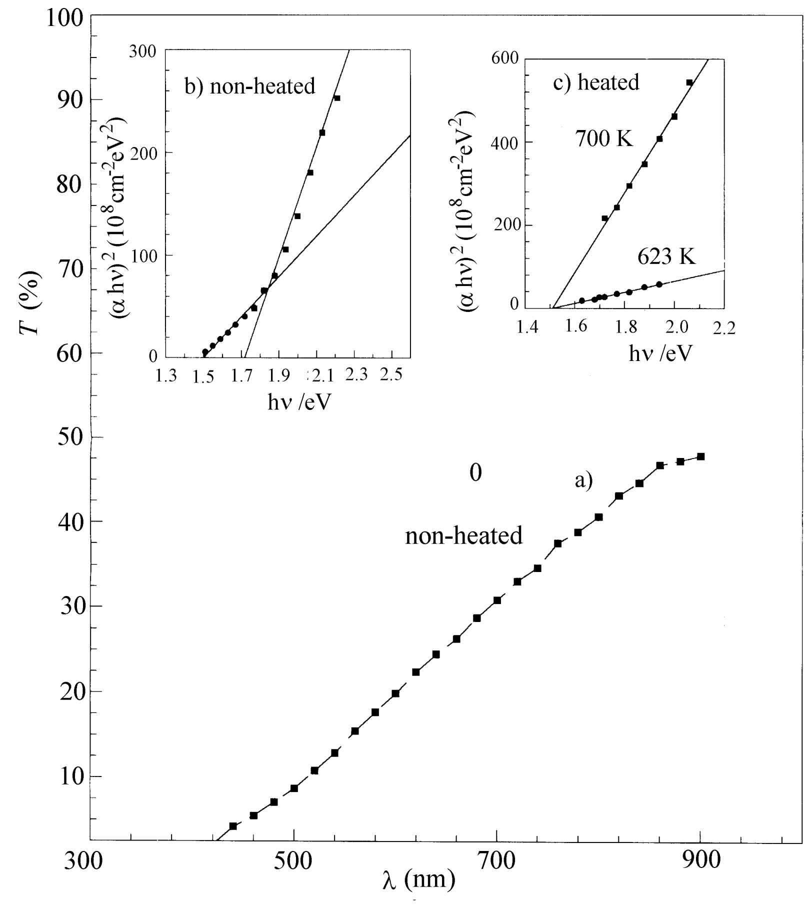

Fig. 4. Plots of a) T vs. λ, b and c) $(\alpha h\nu)^2$ vs. $h\nu$ for thermally deposited $CuInS_2$ *films.*

On the other hand, the thermally as-deposited films demonstrate two optical direct transitions of 1.5 eV and 1.72 eV (Fig. 4b). The energy gap (1.72 eV) is most probably due to the optical transitions from the copper d-states in the valence band to the lowest conduction band minimum which disappeared by heating. This result is confirmed by Neumann et al. [18], where a transition of 1.6 eV - 1.7 eV was assigned to an optical transition from the valence band maximum at or near the boundary of the Brillouin zone (at the points T or N) to the conduction band minimum at the zone centre. The thermally deposited films, heated at 623 K and 700 K in sulfur atmosphere for about 15 minutes, yield a value of 1.52 eV (Fig. 4c) which is greater than the value of 1.5 eV for the non-heated films. The increase in transition for sulfur annealed films has been previously reported. This behaviour is explained as either due to the reduction of the d-level contribution in the upper valence band or the change of lattice distance caused by nature of the native defects [18,19].

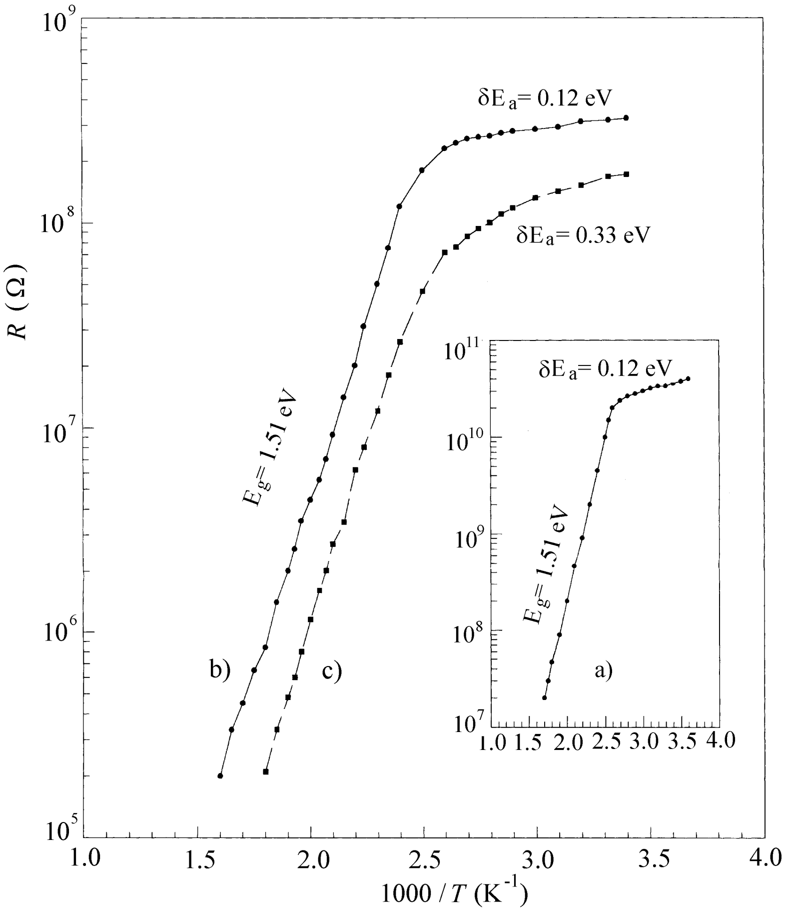

Fig. 5. Plots of $\log R$ *vs.* $1000/T$ *for chemically deposited* $CuInS_2$ *films. a) as-deposited, b) heated to 523* K *and c) heated at 523* K *with excess sulfur.*

The electrical resistance of the as-deposited and annealed chemically prepared films 230 nm thick was measured in the temperature range from 300 K to 673 K as shown in Fig. 5. The presented relation may be divided into two regions, extrinsic and intrinsic. The curves show a decrease in resistivity on annealing under vacuum which is due to the improvement of the crystal quality. On annealing in excess sulfur, the resistivity is still reduced due to addition of more carriers by sulfur interstitials. In the low temperature region (< 373 K), the activation energy for the as-deposited and under vacuum annealed films is 0.12 eV. This may be attributed to some shallow acceptor levels introduced by copper vacancies. Similar work has been done by Look and Manthuruthll [20] on $CuInS_2$ single crystal and they found an acceptor level at 0.15 eV. The predominant defects are sulfur and copper vacancies, but the present specimen is p-type, which implies that the concentration of copper vacancies is greater than that of sulfur. On annealing in excess of sulfur, the activation energy in the low temperature region increases up to 0.33 eV. This is associated with a deep acceptor level created by the interstitial sulfur atoms. It was stated [10] that annealing in excess sulfur removes the donor defects such as In_i and In_{Cu}, leaving the copper vacancy. But since the level is different from the mentioned one (0.15 eV), sulfur interstitials arising after annealing in excess sulfur could be the explanation.

In the high temperature region (intrinsic), the plots of $\ln R$ vs. $1/T$ (Fig. 5) yield a value of 1.51 eV for the energy gap E_g. This value is close to the values obtained from the optical method and it is nearly equal to the values reported earlier using different techniques.

4. Conclusion

The electrical resistance of the as-deposited and annealed chemically-prepared single-phase layers of $CuInS_2$ indicates the extrinsic and intrinsic regions. The annealing in sulfur vapour decreases the resistivity due to a decrease of the lattice defects and an increase of the hole concentration. A direct transition with an optical gap of 1.5 eV was observed. The gap of annealed thermally-prepared films in sulfur is greater than of the as-deposited films, indicating a lesser contribution of the d-level to the valence band.

References

1) L. I. Berger and V. D. Prochukhan, *Ternary Diamond-Like Semiconductors*, Consultant Bureau Enterprises, Inc., New York 1969, p.47;

2) J. D. Meakis, SPIE **543** (1985) 108;

3) J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors*, Pergamon Press, Oxford (1975);

4) G. Masse, N. Lahou and C. Butti, J. Phys. Chem. Solids **42** (1981) 449;

5) B. Tell, J. L. Shay and M. H. Kasper, J. Appl. Phys. **43** (1972) 2469;

6) T. M. Hsu, J. Appl. Phys. **59** (1986) 2538;

7) T. M. Hsu and J. H. Lin, Phys. Rev. **B 37** (1988) 4106;

8) H. Neff. P. Lange, M. L. Fearheiley and K. J. Bachmann, J. Appl. Phys. Lett. **47** (1985) 1089;

9) L. Y. Sun, L. L. Kazmerski, A. H. Clark, P. J. Ireland and D. W. Morton, J. Vac. Sci. Technol. **15** (1978) 265;

10) T. M. Hsu, J. S. Lee and H. L. Hwang, J. Appl. Phys. **68 (1)** (1990) 283;

11) A. N. Y. Samaan, S. M. Wasim, A. E. Hill, D. G. Armour and R. D. Tomlinson, Phys. Stat. Sol. **96 (a)** (1986) 317;

12) P. O. Nilson, Appl. Optics **7** (1968) 435;

13) H. Bihri, C. Messaoudi, D. Sayah, A. Boyer, A. Mzerd and Abd-Lefdil, Phys. Stat. Sol. **(a) 129** (1992) 193;

14) J. J. M. Binsma, L. J. Giling and J. Bloem, J. Cryst. Growth **50** (1980) 429;

15) J. J. M. Binsma and H. A. Vander Linden, Thin Solid Films **97** (1982) 237;

16) G. K. Padam and S. U. M. Rao, Solar Energy Mater. **13** (1986) 297; **15** (1987) 227;

17) G. K. Padam, G. L. Malhotra and S. U. M. Rao, Phys. Stat. Sol. **(a) 109** (1988) K45;

18) H. Neumann, W. Horig, V. Savelev, J. Lagzdonis. B. Schumann and G. Kuhn, Thin Solid Films **79** (1981) 167;

19) H. Nakasnishi, S. Endo, T. Irie and B. H. Chang, *Ternary and Multinary Compounds*, Proceeding of the 7^{th} Int. Conf., edited by S. K. Deb and A. Zunger, Mater. Res. Soc., Pittsburgh, PA, (1987) 99;

20) D. C. Look and J. C. Manthuruthll, J. Phys. Chem. Solids **37** (1976) 173.

PROUČAVANJE KEMIJSKI I TERMIČKI PRIREĐENIH TANKIH SLOJEVA $CuInS_2$

Tanki slojevi bakarnog indij disulfida ($CuInS_2$) priređeni su kemijski i naparavanjem u vakuumu, i istraživana su njihova strukturna, optička i električna svojstva. Rendgenska strukturna analiza pokazuje samo jednofazni kalkopirit bez dodatnih ravnina. Određeni su optički i termički procijepi. Procijep naparenih slojeva, otpuštanih u parama sumpora, veći od procijepa svježe naparenih slojeva. To ukazuje na smanjenje doprinosa d-pojasa valentnom pojasu.