

## **KMDO USULI YORDAMIDA OLINGAN $Sb_2Se_3$ YUPQA QATLAMLARINING STRUKTURAVIY, OPTIK VA ELEKTROFIZIK XUSUSIYATLARI**

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Microstructural, optical and electrical properties of  $Sb_2Se_3$  films fabricated by CMBD method from for Solar Cells

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**Annotatsiya:** Kimyoviy molekulyar dastalar olish (KMDO) metodi tomonidan  $Sb_2Se_3$  yuqori sifatli kristal yupqa qatlamlari  $500^\circ C$  taglik haroratida binar birikmaning  $Sb_2Se_3$  va Se elementining alohida manbalaridan olindi.  $Sb_2Se_3$  yupqa qatlamlarining morfologik, strukturaviy, optik va elektrofizik xossalariga selen manba haroratining ta'siri o'rganildi. Elektron mikroskop tasvirlari va rentgen difraksion analiz ma'lumotlarini asosida olingan barcha yupqa qatlamlar ortorombik polikristal strukturaga va kristall o'lchamlari 5-10 mkm ga ega ekanligi ma'lum bo'ldi. Yupqa qatlamlarning elektr o'tkazuvchanligi Sb/Se atomlari konsentratsiyasi nisbatiga qarab  $1,03 \cdot 10^{-5} \div 4,13 \cdot 10^{-5} (Om \cdot sm)^{-1}$  oraliqda bo'lishi aniqlandi.

**Kalit so'zlar:**  $Sb_2Se_3$ , KMDO, yupqa qatlamlar, harorat, struktura, morfologiya, rentgen difraksion ta'svir, elektr o'tkazuvchanlik, absorbsiya koeffitsienti.

**Abstract.** Highly crystalline  $Sb_2Se_3$  films were obtained by chemical molecular beam deposition (CMBD) method from separate sources of  $Sb_2Se_3$  binary compound and Se elements, at a substrate temperature of  $500^\circ C$ . The effect of source of selenium temperature on the morphological, structural, optical and electrical properties of  $Sb_2Se_3$  films has been studied. On the basis of scanning electron microscope images and X-ray diffraction data, it was revealed, that all films have a polycrystalline orthorhombic structure, and the crystallite size is 5-10  $\mu m$ . The electrical conductivity of the films, changed within  $1,03 \cdot 10^{-5} \div 4,13 \cdot 10^{-5} (Om \cdot cm)^{-1}$  depending on the ratio of Sb/Se atomic concentration.

**Keywords:**  $Sb_2Se_3$ , CMBD, thin films, temperature, structure, morphology, X-ray diffraction pattern, electrical conductivity, absorption coefficient.

### **Kirish**

Yupqa qatlamli quyosh elementlarining samaradorligi asosan asosiy qatlamning fizik xususiyatlari bilan bog'liq. Hozirgi vaqtda quyosh elementlarida asosiy qatlamni olishning vakuumsiz, yuqori va past vakuumli usullari qo'llaniladi. Quyosh

elementining asosiy qatlamining fizik xususiyatlari usullarning texnologik parametrlariga sezilarli darajada bog'liq.

Bugungi kunda Si, a-Si, CdTe, Cu(In, Ga)(Se, S)<sub>2</sub> materiallariga asoslangan quyosh xujayralari keng tarqalgan. Ularning erishilgan samaradorligi quyidagi qiymatlarga ega: Si  $\eta=26,7\%$  (lab.),  $\eta=24,4\%$ , (modul); a-Si  $\eta=14\%$  (lab.),  $\eta=12,3\%$ , (modul); CdTe-  $\eta=22,1\%$  (lab.),  $\eta=19\%$ , (modul); Cu(In,Ga)(Se,S)<sub>2</sub>,  $\eta=23,4\%$  (lab.),  $\eta=19\%$ , (modul), mos ravishda.

Shu bilan birga, turli kompaniyalar Si, a-Si, CdTe, Cu(In,Ga)(Se,S)<sub>2</sub> quyosh batareyalari asosida 310–450 Vt quvvatga ega quyosh modullarini ishlab chiqarishni yo'lga qo'ydilar. Ishlab chiqarilgan quyosh modullarining 95% silikon quyosh batareyalaridir. 2021-yilga kelib mono-Si, poli-Si va yupqa qatlamli quyosh elementlari modullarga asoslangan quyosh fotoelektr stantsiyalari 120,6 GVt, 23,3 GVt va 7,7 GVt quvvatga ega. Fotovoltaik stantsiyalar tomonidan ishlab chiqarilgan energiya butun dunyo bo'ylab olinadigan umumiy energiyaning 3,3% ni tashkil qiladi. Shunga qaramay, quyosh batareyalari uchun ishlatiladigan ushbu materiallarning ba'zi kamchiliklari tufayli Gega va TeraW shkalalarida quyosh modullarini keng ishlab chiqarish cheklangan.

Quyosh elementlari uchun asosiy material sifatida Si dan foydalanishning asosiy kamchiliklari quyidagilardir:

- kremniyning taqiqlangan soha kengligi (1,1 eV), bu optimal qiymatdan 1,4-1,6 eV [3] dan kam, past assimilyatsiya koeffitsienti ( $\sim 10^2 \text{ sm}^{-1}$ ).

Shuning uchun kattaroq qalinlikdagi (100-200 mkm) materialdan foydalanish kerak, bu esa yakuniy mahsulot narxining oshishiga olib keladi.

Shu bilan birga, Cu(In,Ga)Se<sub>2</sub> va CdTe asosidagi yupqa qatlamli quyosh batareyalaridan yanada keng foydalanish yer qobig'idagi In, Ga, Te ning cheklangan zahiralari va kadmiyning zaharliligi tufayli katta qiyinchiliklar tug'diradi.

Ekologik muammolarni, shuningdek, ommaviy ishlab chiqarish uchun materiallar etishmasligi bilan bog'liq muammolarni bartaraf etish uchun Cu<sub>2</sub>ZnSnS<sub>4</sub>(CZTS) absorber qatlamiga asoslangan yangi quyosh batareyasi Cu(In, Ga)(Se, S)<sub>2</sub>, bu yerda indiy va galiy o'rni sink (Zn) va qalay (Sn) egallaydi, ular yer qobig'ida ancha ko'p. Shu bilan birga, ushbu elementlarning afzalligi ularning arzonligi (tabiatda tarqalishi) va toksik emasligidir. Cu<sub>2</sub>ZnSnS<sub>x</sub>Se<sub>4-x</sub> - x asosidagi quyosh batareyalarining samaradorligi IBM tadqiqot markazi tomonidan 12,6% gacha erishilgan. Biroq, bu samaradorlik Cu(In,Ga)(Se,S)<sub>2</sub> dan ancha past. Tadqiqotlarga ko'ra, past samaradorlikka ega yupqa qatlamli quyosh elementlari tarkibini olish va nazorat qilish usulining murakkabligi bilan izohlanadi. Hozirgi vaqtda jahon tadqiqotchilari quyosh elementlari uchun yutuvchi qatlam sifatida ular asosidagi xalkogenidli binar birikmalar Sb<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>S<sub>3</sub> va Sb<sub>2</sub>(S<sub>x</sub>,Se<sub>1-x</sub>)<sub>3</sub> qattiq eritmalaridan (kimyoviy formula Sb<sub>2</sub>X<sub>3</sub>) foydalanishga alohida e'tibor qaratmoqda. Buning sababi, fizik xossalari p-tipli

o'tkazuvchanlik, taqiqlangan soha kengligi  $E_g=1,1\div 1,8$  eV, yuqori yutilish koeffitsienti  $\alpha > 10^5 \text{sm}^{-1}$  (quyosh radiatsiyasining ko'rinadigan hududida), past erish nuqtasi ( $\text{Sb}_2\text{Se}_3$ -823K,  $\text{Sb}_2\text{S}_3$ -885K) va bu materiallarning xossalari  $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$  xossalari juda yaqin. Bundan tashqari, ushbu materiallarga kiritilgan elementlar nisbatan past narxga (tabiatda tarqalishi) ega, tashqi ta'sirlarda barqaror va toksik emas. Bu ekologik toza va samarali quyosh modullarini ishlab chiqarish imkonini beradi, shuningdek, ularni sanoat miqyosida keng ishlab chiqarish yo'llarini ochadi.

Ushbu keltirilgan ma'lumotlarga asosan tadqiqotning maqsadi kimyoviy molekulalar dastalaridan olish (KMDO) usuli bilan turli tarkibli  $\text{Sb}_2\text{Se}_3$  yupqa qatlamini olishning optimal texnologik sharoitini aniqlash va ularning morfologik, strukturaviy, optik va elektrofizik xossalarini tadqiq etish talab etilayotgan muhim vazifalardandir.

### Эксперимент

Bu ilmiy ishning maqsadi, turli miqdorda Se elementi bilan boyitilgan  $\text{Sb}_2\text{Se}_3$  yupqa qatlamlarining morfologik va strukturaviy xususiyatlarini tadqiq etish. Boshlang'ich material sifatida  $\text{Sb}_2\text{Se}_3$  kukuni (99.999 %) va toza Se elementi ishlatilgan bo'lib, ular kimyoviy molekulyar dastalarda olish (KMDO) usuli bilan vodorod atmosfera bosimida olingan. Vodorod gazining oqimi  $20 \text{sm}^3/\text{min}$ .  $\text{Sb}_2\text{Se}_3$  binar birikmasining bug'lanish harorati o'zgarimas  $800^\circ\text{C}$  da va Se elementining bug'lanish harorati ( $350^\circ\text{C}$ ,  $370^\circ\text{C}$ ,  $390^\circ\text{C}$ ,  $410^\circ\text{C}$ ,  $430^\circ\text{C}$ ), oraliqlarda o'zgartirilib borildi. Taglik harorati doimiy  $500^\circ\text{C}$  haroratda saqlandi. Tajriba davomiyligi yupqa qatlamlarning qalinligiga bog'liq va 30 daqiqa davom etdi. Ohakli natriy shishalari va molibden shisha qatlamlari taglik sifatida ishlatildi. Olingan namunalarning o'lchamlari  $2,0 * 2,0 \text{sm}^2$ . Selenga boy va stexiometrik kompozitsion  $\text{Sb}_2\text{Se}_3$  yupqa qatlamlarini olish uchun o'sish jarayonida bug' fazasida Se ning qisman bosimi o'zgartirildi.

### Natijalar tahlili

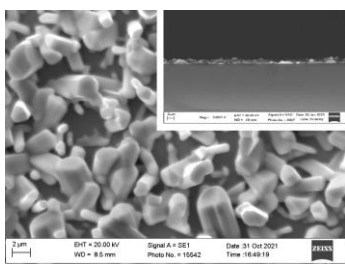
Se ning turli harorat diapazonlarida skanerlovchi elektron mikroskop yordamida olingan  $\text{Sb}_2\text{Se}_3$  yupqa qatlamlarining sirt va kesma tasvirlari ko'rsatilgan.  $\text{Sb}_2\text{Se}_3$  binar birikmasi nisbatan o'zgarmagan. 1-rasmdan ko'rinib turibdiki, barcha  $\text{Sb}_2\text{Se}_3$  qatlamlari uchun mikrokristallar taglik yuzasida bir xilda taqsimlangan. Bundan tashqari, yupqa plyonka yuzasi Se ning birgalikda bug'lanishi natijasida silliqroq va ixchamroq bo'ldi. 1-rasmda ko'rsatilganidek, mikrostruktura (kristallitlarning shakli va hajmi) va namunalarning qalinligi plyonkalar tarkibiga bog'liq.

Namunalar kesmasining skanerlangan elektron mikroskop tasvirlari shuni ko'rsatdiki, yaqin stexiometrik tarkibli plyonkalar 30 daqiqa davomida cho'kish jarayonida olingan qalinligi  $1\div 3$  mkm bo'ldi. Bu plyonka qalinligi selen tarkibiga bog'liqligini anglatadi.  $T_{\text{Se}}=350^\circ\text{C}$  boshlang'ich haroratda (1-rasm, a) diametrli  $d=1 - 2$  mkm va uzunligi  $l=3-5$  mkm bo'lgan mikrotayoqchalar ko'rinishidagi kristallitlarning o'sishi sezilarli siljish burchagi bilan kuzatiladi.  $T_{\text{Se}}=370^\circ\text{C}$  (1-rasm, b) va  $T_{\text{Se}}=390^\circ\text{C}$

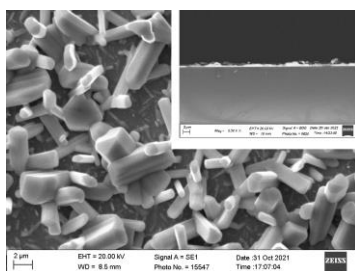
(1-rasm, c) da olingan plyonkalar bir-biridan deyarli farq qilmaydi, shu bilan birga kristallitlarning uzunligi biroz oshadi va taxminan 5-10 mkm ni tashkil qiladi, kristallitlarning diametri ~ 2 mkm ga etadi.

Shu bilan birga, selen  $T_{Se}=350^{\circ}S \div 390^{\circ}C$  haroratda yotqizilgan namunalar uchun sezilarli miqdordagi kristallararo bo'shliqlar va kristallitlarning past ixchamligi aniqlandi. Bu plyonkalar sifatsiz kristall shaklga ega ekanligini ko'rsatadi. Selen manbasining berilgan harorati namunalari uchun plyonka qalinligi ~1 mkm (1-rasm a.b.c. kesmaning SEM tasviri).

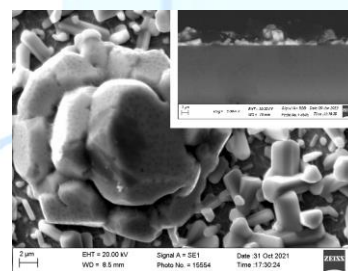
Yupqa qatlamlar yuzasida selen manbai  $T_{Se}=410^{\circ}C$  va  $T_{Se}=430^{\circ}C$  haroratining yanada oshishi kristallararo bo'shliqlar yo'qligini va o'sish yo'nalishi boshqacha bo'lgan kristallitlarning yuqori tartiblilikini ko'rsatdi. Kengaytirilgan mikrorodlar shaklidagi kristallarning uzunligi 10-15 mkm, diametri esa 2-3 mkm (1-rasm d,e.). Selen manbai  $T_{Se}=410^{\circ}C$  va  $T_{Se}=430^{\circ}C$  haroratida o'stirilgan yupqa qatlamlar qalinligi ~3 mkm (1-rasm d,e kesmaning SEM tasviri).



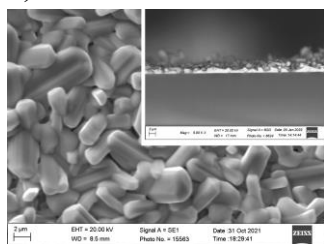
a)  $T_{Se}=350^{\circ}C$



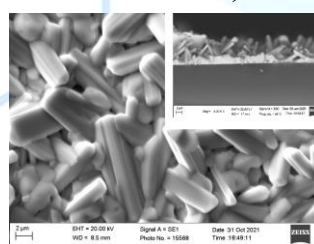
b)  $T_{Se}=370^{\circ}C$



c)  $T_{Se}=390^{\circ}C$



d)  $T_{Se}=410^{\circ}C$



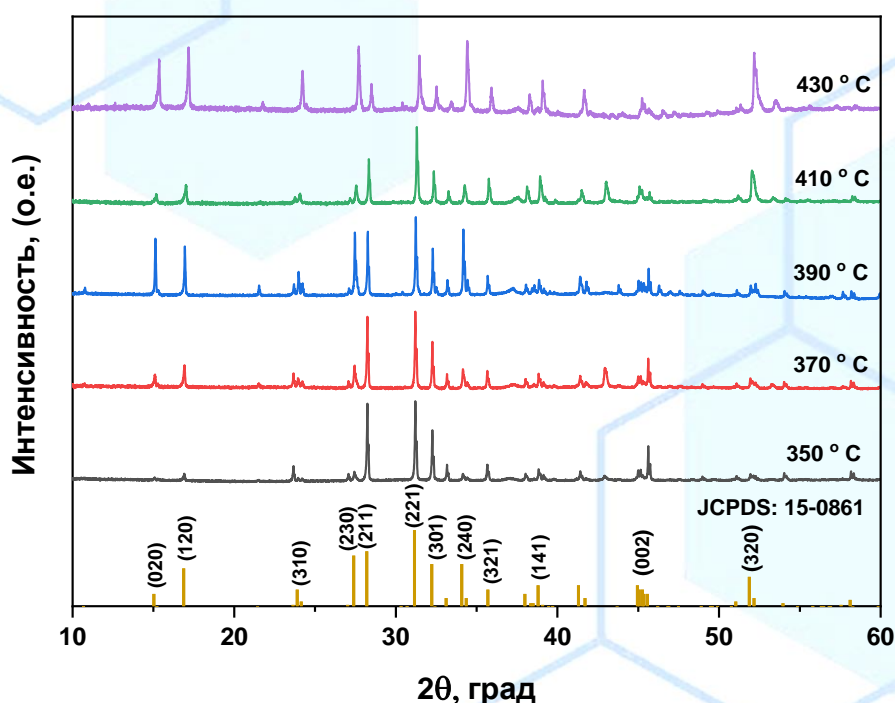
e)  $T_{Se}=430^{\circ}C$

*1-rasm. Selen manbasining turli haroratida skanerlovchi elektron mikroskopda olingan  $Sb_2Se_3$  yupqa plyonkalarining morfologiyasi.*

KMDO usulida o'stirilgan  $Sb_2Se_3$  yupqa qatlamlari elementlarining kimyoviy tarkibi 1-jadvalda keltirilgan. Bu jadvaldan ko'rinib turibdiki, Se ning harorati  $350^{\circ}C$  dan  $430^{\circ}C$  gacha ko'tarilishi bilan Sb/Se ning atom konsentratsiyasining nisbati pasayadi va Sb/Se ning 0,67 [21] stexiometrik tarkibiga yaqinlashadi. Ya'ni, bu natijalar  $Sb_2Se_3$  yupqa plyonkalaridagi Se tarkibining Se oqimining oshishi bilan ortganligini ko'rsatadi.

*$Sb_2Se_3$  plyonkasining kimyoviy tarkibi*

№	T <sub>Se</sub> (Se harorati)	Sb (atom ulushi %)	Se (atom ulushi %)	Sb/Se (atom nisbati)
1	350	43,80	56,20	0,78
2	370	43,89	56,11	0,78
3	390	43,10	56,90	0,76
4	410	42,15	57,85	0,73
5	430	41,65	58,35	0,71



2-rasm. Se manbasining turli haroratlarida olingan  $Sb_2Se_3$  yupqa qatlamlarining rentgenogrammalari

2-rasmda o'sish jarayonida turli xil Se ning harorat diapazonlarida olingan  $Sb_2Se_3$  plyonkalarining rentgen nurlanishining diffraksiyasi ko'rsatilgan. Rentgen nurlari difraksion tahlil natijalari shuni ko'rsatadiki, barcha plyonkalar polikristalli ortorombik tuzilishga ega. Rasmdan ko'rinib turibdiki, rentgen nurlarining diffraksiya shakllarida asosiy kuchli cho'qqilar (221), (211) va ikkilamchi zaif cho'qqilar (020), (120) va (310) kuzatiladi, ular Se ning haroratiga qarab sezilarli darajada o'zgaradi.  $T_{Se}=350^{\circ}C-390^{\circ}C$  harorat oralig'ida ikkita kuchli cho'qqi (221), (211) va zaif cho'qqilar (020), (120), (310), (230), (240), (002) kuzatiladi. (320) cho'qqi  $T_{Se}=370^{\circ}C$  gacha bo'lgan haroratlarda amalda ko'rinmaydi. Shu bilan birga,  $T_{Se}=390^{\circ}C$  haroratda namunalar uchun rentgenogrammalarda zaif cho'qqilar (020), (120), (230), (240) sezilarli darajada namoyon bo'ladi. Bu shuni anglatadiki, kristall o'sishi ushbu yo'nalishlarda o'sishni boshlaydi. Haroratning yana  $T_{Se}=410^{\circ}C$  gacha ko'tarilishi bilan kuchli cho'qqilarning

intensivligi (221) o'zgaraydi, (211) esa pasayadi.  $T_{se}=430^{\circ}C$  haroratda cho'qqilarning (221), (211) pasayishiga va zaif cho'qqilarning (020), (120), (230), (240) sezilarli darajada oshishiga olib keladi. Yuqorida aytilganlarga asosan,  $T_{se}=410^{\circ}S$  dan  $T_{se}=430^{\circ}S$  gacha bo'lgan haroratda olingan  $Sb_2Se_3$  plyonkalar uchun yaxshilangan kristall tuzilmalari mavjudligi aniqlandi, bunda katta kristalit o'lchamli ( $l=10\div 15$  mkm) plyonkalarining eng yaxshi morfologiyasi mavjud (diametri  $d=2\div 3$  mkm), oraliq bo'shliqlarsiz va yuqori ixchamlik bilan hosil bo'ladi, bu esa o'z navbatida plyonkalarining elektr va optik xususiyatlarining yaxshilanishiga olib keladi.

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