



4O10Cd Clustering in Zn B^{VI} -Rich Cd $_x$ Zn $_{1-x}$ O $_y$ B $_{1-y}^{VI}$ (B^{VI} = S, Se, Te) Highly Lattice-Mismatched Alloys

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Clustering of highly lattice-mismatched semiconductor alloys has attracted considerable interest recently. However, strong internal strains and cluster variety are the main disadvantages of such alloys. Zinc blende Zn B^{VI} -rich Cd $_x$ Zn $_{1-x}$ O $_y$ B $_{1-y}^{VI}$ (B^{VI} = S, Se, Te) with 4O10Cd identical clusters are proposed to resolve these problems. The decrease in the internal strains is a cause of the cluster formation in ZnS- and ZnSe-rich alloys. The favorable CdO and ZnTe bonding is an additional reason for the cluster occurrence in ZnTe-rich alloys. The cohesive energies of CdSe and ZnSe, stiffness coefficients, bond stretching and bond bending elastic constants of CdSe are calculated. The majority of Cd and oxygen atoms should be in 4O10Cd clusters up to 800°C if the ZnS- and ZnSe-rich alloy contents are, respectively, $y \geq 2.5 \times 10^{-4}$ and $y > 3 \times 10^{-4}$, and $x \approx 2.5y$. The obtained results demonstrate that Cd $_x$ Zn $_{1-x}$ O $_y$ B $_{1-y}^{VI}$ materials are promising semiconductors with significantly reduced internal strains and identical polyatomic clusters containing oxygen tetrahedrons.

Key words: II-VI Semiconductors, quaternary alloys, self-assembly, identical 4O10Cd clusters

INTRODUCTION

Highly lattice-mismatched semiconductor alloys such as oxides, nitrides and bismides are widely studied now.^{1–5} This is mainly due to the possibility of band gap engineering and clustering properties of these semiconductors. However, clusters are normally not identical, as was established in the late 1960s for nitrogen dyads in GaP:N.⁶ Moreover, clusters with highly size-mismatched atoms cause significant crystal lattice strains. The 1O4Cd cluster formation under which the internal strains in highly mismatched ZnTe-rich Cd $_x$ Zn $_{1-x}$ O $_y$ Te $_{1-y}$ alloys decrease has been described.⁷ This is due to the fact that Cd and oxygen atoms are larger and smaller, respectively, than Zn and Te atoms. Identical 1O4Cd clusters are Cd tetrahedrons with oxygen atoms in their centers. Such clustering is

favorable because the cluster occurrence significantly compensates the internal strains caused by isolated Cd and oxygen atoms in the ZnTe-rich matrix. It was later shown that polyatomic identical 4B10Sb clusters are more preferred than that of 1B4Sb in GaAs-rich B $_x$ Ga $_{1-x}$ Sb $_y$ As $_{1-y}$ highly mismatched alloys.⁸ 4B10Sb clusters are boron tetrahedrons surrounded by Sb atoms. The significant decrease in the internal strains in Cd $_x$ Zn $_{1-x}$ O $_y$ Te $_{1-y}$ and in B $_x$ Ga $_{1-x}$ Sb $_y$ As $_{1-y}$ after the cluster occurrence^{7,8} allows us to expect the 4O10Cd and 1O4Cd cluster formation in Zn B^{VI} -rich Cd $_x$ Zn $_{1-x}$ O $_y$ B $_{1-y}^{VI}$ (B^{VI} = S, Se, Te). The cluster formation in the Zn B^{VI} -rich alloys should be a result self-diffusion processes of mismatched atoms. As shown in^{9,10} annealing at 670°C yields dissolution of In-rich islands and N-rich clusters in In $_x$ Ga $_{1-x}$ N $_y$ As $_{1-y}$ epitaxial films. Thus, annealing is an effective method to compensate the internal strains due to changes in the crystal structure of the quaternary semiconductor alloys. ZnO $_y$ S $_{1-y}$ is the least mismatched among ZnO $_y$ B $_{1-y}^{VI}$ (B^{VI} = S, Se, Te) alloys.

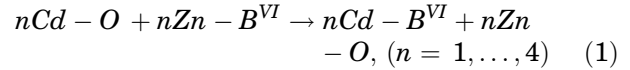
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However, the defect emissions of $\text{ZnO}_y\text{S}_{1-y}$ crystals with $y = 0.06$ and 0.12 were established.¹¹ Photoluminescence spectra from chemical vapor-deposited $\text{ZnS}:\text{O}$ are shown to exhibit sub-band-gap emission bands characteristic of isoelectronic oxygen defects. The emission spectra vary spatially with position and orientation with respect to the major axis of growth. These data suggest that a complex set of defects exist in the band gap of $\text{ZnS}:\text{O}$ whose structural nature is highly dependent upon local deposition and growth conditions, contributing to inherent heterogeneity in optical behavior throughout the material.¹² Thus, the emission characteristics correspond to the different O-rich clusters in $\text{ZnS}:\text{O}$. Studies of the low-temperature photoluminescence emission from $\text{ZnSe}_{1-y}\text{O}_y$ alloys with an oxygen content varying from 0 to 1.35% were presented in.² Two emission bands related to localized and free exciton recombination had been identified by the comparison with photoreflectance. The measurements reveal that the localized emission band is composed of a series of narrow emission lines that can be attributed to the recombination of single excitons trapped by potential fluctuations. The presented results demonstrate that the studied $\text{ZnSe}_{1-y}\text{O}_y$ epitaxial films contain different highly mismatched O-rich clusters. As shown in,¹³ an addition of Cd atoms improves the optical quality of ZnTe-rich $\text{ZnO}_y\text{Te}_{1-y}$ alloys. Apparently, this improvement is due to the transformation of $\text{ZnO}_y\text{Te}_{1-y}$ alloys in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Te}_{1-y}$ alloys with the reduced internal strains caused by mismatched atoms. Thus, the study of ways to reduce internal strains in the highly mismatched alloys due to the formation of identical clusters is a very important problem. The identical cluster formation conditions in zinc blende ZnB^{VI} -rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{B}_{1-y}^{\text{VI}}$ ($\text{B}^{\text{VI}} = \text{S}, \text{Se}, \text{Te}$) alloys are presented here.

MODEL

ZnB^{VI} ($\text{B}^{\text{VI}} = \text{S}, \text{Se}, \text{Te}$) semiconductors crystallize with the zinc blende structure. Therefore, the ZnB^{VI} -rich alloys in which mismatched atoms are in the dilute limits also should have the zinc blende structure. Clustering in zinc blende ZnB^{VI} -rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{B}_{1-y}^{\text{VI}}$ ($\text{B}^{\text{VI}} = \text{S}, \text{Se}, \text{Te}$) is presented by using the 4O10Cd and 1O4Cd cluster order parameters α (4O10Cd COP) and β (1O4Cd COP), respectively. 4O10Cd and 1O4Cd COPs are the ratios between numbers of oxygen atoms in 4O10Cd and 1O4Cd clusters, correspondingly, and the total number of oxygen atoms. 4O10Cd clusters are oxygen tetrahedrons surrounded by Cd atoms. The cluster formation is favored if it decreases the free energy. The free energy is presented as a sum of the bond energy, internal strain energy and entropy term $f = u^B + u^{\text{IS}} - Ts$. ZnB^{VI} -rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{B}_{1-y}^{\text{VI}}$ are alloys of CdO, CdB^{VI} , ZnO and ZnB^{VI} constituent compounds corresponding to the chemical bonds in them. Each atom in these alloys may have

the different nearest neighbors as both sublattices of the crystal structure are mixed. Therefore, the bond energy depends on the arrangement of atoms since an exchange of lattice sites between cations or anions may result in the transformation of chemical bonds



or vice versa. The bond energy is

$$u^B = \Delta u_{\text{B}^{\text{VI}}}^B (\alpha + \beta)(1-x)y + \Delta u_{\text{B}^{\text{VI}}}^B xy + u_{\text{ZnB}^{\text{VI}}}^B + (u_{\text{CdB}^{\text{VI}}}^B - u_{\text{ZnB}^{\text{VI}}}^B)x + (u_{\text{ZnO}}^B - u_{\text{ZnB}^{\text{VI}}}^B)y, \quad (2)$$

where $\Delta u_{\text{B}^{\text{VI}}}^B = u_{\text{CdO}}^B - u_{\text{CdB}^{\text{VI}}}^B - u_{\text{ZnO}}^B + u_{\text{ZnB}^{\text{VI}}}^B$ and u_{CdO}^B is the bond energy of zinc blende CdO. The change of the sum (2) under variations of 4O10Cd and 1O4Cd COPs depends only on the first item. Therefore, only it will be taken into account later on. The value of $\Delta u_{\text{B}^{\text{VI}}}^B$ is equal to the negative value of the similar relation between the cohesive energies of the same compounds $\Delta u_{\text{B}^{\text{VI}}}^{\text{Coh}} = u_{\text{CdO}}^{\text{Coh}} - u_{\text{CdB}^{\text{VI}}}^{\text{Coh}} - u_{\text{ZnO}}^{\text{Coh}} + u_{\text{ZnB}^{\text{VI}}}^{\text{Coh}}$ since the energies of atoms involved in the cohesive energies are self-cancelled. The relations between the cohesive energies of the constituent compounds of zinc blende ZnS-rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$ and ZnTe-rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Te}_{1-y}$ are $\Delta u_{\text{S}}^{\text{Coh}} = 16 \text{ kJmol}^{-1}$ and $\Delta u_{\text{Te}}^{\text{Coh}} = -37 \text{ kJmol}^{-1}$, respectively.^{7,14} These relations demonstrate that the CdS and ZnO bondings are insignificantly favorable in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$, but in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Te}_{1-y}$, the CdO and ZnTe bondings are preferred.

The cohesive energy of ZnSe was obtained as $u_{\text{ZnSe}}^{\text{Coh}} = -h_{\text{ZnSe}}^{\text{of}} + u_{\text{Zn}}^{\text{At}} + u_{\text{Se}}^{\text{At}} = 0.508 \text{ MJmol}^{-1}$, where $h_{\text{ZnSe}}^{\text{of}}$ is the enthalpy of formation of zinc blende ZnSe,¹⁵ $u_{\text{Zn}}^{\text{At}}$ and $u_{\text{Se}}^{\text{At}}$ are the atomization energies of Zn and Se, respectively, taken from.¹⁶ The difference between the cohesive energies of the same compound with different crystal structures depends mainly on the coordination number, distance between atoms and Madelung constant.¹⁷ The distances between atoms in the wurtzite and zinc blende allotropic forms of a compound as well as the Madelung constants are almost equal.¹⁸ Thus, the difference between the cohesive energies of a compound with the wurtzite and zinc blende structures should not be large. Therefore, the cohesive energies of wurtzite ZnO ¹⁹ and CdSe were used in the calculations. The cohesive energy of wurtzite CdSe was obtained as $u_{\text{CdSe}}^{\text{Coh}} = -h_{\text{CdSe}}^{\text{of}} + u_{\text{Cd}}^{\text{At}} + u_{\text{Se}}^{\text{At}} = 0.456 \text{ MJmol}^{-1}$, where $h_{\text{CdSe}}^{\text{of}}$ is the enthalpy of formation of wurtzite CdSe from,¹⁵ $u_{\text{Cd}}^{\text{At}}$ and $u_{\text{Se}}^{\text{At}}$ are the atomization energies of Cd and Se, respectively. The relation between the cohesive energies of the compounds of $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Se}_{1-y}$ was estimated as $\Delta u_{\text{Se}}^{\text{Coh}} = 25 \text{ kJmol}^{-1}$. This relation demonstrates that the CdSe and ZnO bonding are favorable in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Se}_{1-y}$.

The internal strain energy of Cd_xZn_{1-x}O_yB_{1-y}^{VI} is given by

$$\begin{aligned}
 u^{IS} = & (1 - \alpha - \beta)y u_{O(\text{ZnB}^{VI})} \\
 & + (x - 2.5\alpha y - 4\beta y) u_{Cd(\text{ZnB}^{VI})} \\
 & + 0.25\alpha y u_{4O10Cd(\text{ZnB}^{VI})} + \beta y u_{1O4Cd(\text{ZnB}^{VI})}, \quad (3)
 \end{aligned}$$

where $u_{O(\text{ZnB}^{VI})}$, $u_{Cd(\text{ZnB}^{VI})}$, $u_{4O10Cd(\text{ZnB}^{VI})}$ and $u_{1O4Cd(\text{ZnB}^{VI})}$ are the strain energies due to isolated mismatched atoms and clusters in the ZnB^{VI}-rich alloy, correspondingly. These energies were calculated as sums of two terms. The first term is the energies caused by the distortions of bonds and angles between bonds formed by Cd or oxygen atoms or both of them. This part is described by using the valence force field model.²⁰ The bond stretching and bond bending elastic constants of zinc blende CdO, CdS, CdTe, ZnS, ZnSe and ZnTe are shown in Table I. The elastic constants were taken from.^{7,14,20} The bond stretching and bond bending elastic constants of zinc blende CdSe were estimated by using its stiffness coefficients and distance between the nearest neighbors. The stiffness coefficients of CdSe equal to $C_{11}^{\text{CdSe}} = 53.6\text{GPa}$, $C_{12}^{\text{CdSe}} = 37.0\text{GPa}$ and $C_{44}^{\text{CdSe}} = 19.9\text{GPa}$ were calculated by using the model.²¹ The distance between the nearest neighbors in zinc blende CdSe was taken from.²² The second terms of the sums are the deformation energies of ZnB^{VI}-rich matrixes. The estimated internal strain energies due to isolated Cd and oxygen atoms, 1O4Cd and 4O10Cd clusters in Cd_xZn_{1-x}O_yS_{1-y}, Cd_xZn_{1-x}O_ySe_{1-y} and Cd_xZn_{1-x}O_yTe_{1-y} are shown in Table II. The obtained values of the energies demonstrate the favorable 4O10Cd clustering from the internal strain energy standpoint. Therefore, the alloys with $y/x \approx 2.5$ were considered since, in such case, the majority of mismatched atoms may be in 4O10Cd clusters.

A cluster occurrence decreases the entropy. Therefore, the change of the entropy after the cluster formation was taken into account. The entropy term is

$$\begin{aligned}
 -Ts = & RT(1 - \alpha)y \ln \frac{(1 - \alpha)y}{1 - \alpha y} + RT(1 - y) \ln \frac{1 - y}{1 - \alpha y} \\
 & + RT \left(x - \frac{10}{4}\alpha y - 4\beta y \right) \ln \frac{x - \frac{10}{4}\alpha y - 4\beta y}{1 - \frac{10}{4}\alpha y - 4\beta y} \\
 & + RT(1 - x) \ln \frac{1 - x}{1 - \frac{10}{4}\alpha y - 4\beta y} \\
 & + RT(1 - \alpha - \beta)y \ln \frac{1 - \alpha - \beta}{1 - \alpha} + RT\beta y \ln \frac{\beta}{1 - \alpha} \\
 & + \frac{1}{10}RT\alpha y \ln \frac{27\alpha y}{20} + \frac{2}{27}RT \ln \frac{20 - 27\alpha y}{20} \quad (4)
 \end{aligned}$$

The entropy was obtained as a function of a number of different atomic configurations. This number is presented as a product of two factors. The first factor is the number of permutations of atoms when isolated Cd and oxygen as well as 1O4Cd clusters are distributed randomly at a fixed location of 4O10Cd clusters. The second factor is a number of the arrangements of 4O10Cd clusters. The values of COPs were calculated by minimization of the free energy.

RESULTS AND DISCUSSION

The ZnB^{VI}-rich epitaxial films are, normally, grown at low temperatures. The 4O10Cd and 1O4Cd cluster formation during low-temperature

Table II. The estimated deformation energies caused by isolated mismatched atoms and clusters

For atoms (kJmol ⁻¹)		For clusters (kJmol ⁻¹)	
$u_{Cd(\text{ZnS})}$	$u_{O(\text{ZnS})}$	$u_{1O4Cd(\text{ZnS})}$	$u_{4O10Cd(\text{ZnS})}$
24.983	58.911	58.6102	57.243
$u_{Cd(\text{ZnSe})}$	$u_{O(\text{ZnSe})}$	$u_{1O4Cd(\text{ZnSe})}$	$u_{4O10Cd(\text{ZnSe})}$
6.225	77.721	97.604	101.656
$u_{Cd(\text{ZnTe})}$	$u_{O(\text{ZnTe})}$	$u_{1O4Cd(\text{ZnTe})}$	$u_{4O10Cd(\text{ZnTe})}$
6.063	162.03	137.02	389.95

Table I. The bond bending and bond stretching elastic constants taken from Refs. 7,14 and 20

	Bond stretching constants (N/m)	Bond bending constants (N/m)
ZnO	51.32	11.60
ZnS	44.92	4.78
ZnSe	35.24	4.23
ZnTe	31.35	4.45
CdO	34.20	4.80
CdS	35.15	3.59
CdSe	27.29	2.21
CdTe	29.02	2.43

growth may be unlikely since the oxygen and Cd diffusion in the crystal lattice is necessary for such processes. High-temperature annealing of the alloy films can be an effective method to change the arrangement of atoms over long distances, as was demonstrated for $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$ epitaxial films.^{9,10} $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{B}_{1-y}^{\text{VI}}$ belongs to the same type of alloys as $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}$. That is why the temperatures up to 800°C were considered. Alloys with the clusters formed by high-temperature annealing should be in the “frozen” state at room temperature (RT). However, the self-diffusion processes that may change COPs are very slow at RT, and, therefore, the alloys with the clusters may be used for device applications.

Single crystals of ZnS-rich $\text{ZnO}_y\text{S}_{1-y}$ have been successfully grown by a chemical vapor transport method with oxygen content up to $y = 0.12$.¹¹ Therefore, the compositions of ZnS-rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$ with $y \geq 1 \times 10^{-4}$ and $x \approx 2.5y$ were considered. Although the 104Cd cluster formation decreases the free energy, the occurrence of 4O10Cd clusters in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$ is preferred from a thermodynamics standpoint. The temperature dependence of 4O10Cd COPs for $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$ with $y = 5 \times 10^{-4}$, 4×10^{-4} , 3×10^{-4} and $x = 2.5y$ is shown in Fig. 1. Such contents may be used if small cluster densities are desired. The decrease in the strain energy after cluster formation may be almost 2.7 times if almost all mismatched atoms are in 4O10Cd clusters. The temperature dependence of 4O10Cd COPs for $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$ with $y = 5 \times 10^{-4}$, 4×10^{-4} , 3×10^{-4} and $x = 2.5y$ is shown in Fig. 1. Such contents may be used if small cluster densities are desired. As was established for $\text{ZnO}_y\text{S}_{1-y}$, the iso-electronic oxygen defects exhibited sub-band-gap emission if the oxygen content is in the dilute limit.¹² Such defects, except oxygen substitutional atoms, contain zinc interstitials and zinc vacancies. It seems reasonable that zinc interstitials and zinc vacancies

should be improbable in ZnS-rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$ with 4O10Cd clusters due to the internal strain compensation.

The luminescence properties of $\text{ZnO}_y\text{Se}_{1-y}$ films grown by molecular beam epitaxy with the oxygen content up to 1.35% were studied in.² The low-temperature broad photoluminescence spectrum of ZnSe-rich $\text{ZnO}_y\text{Se}_{1-y}$ attributed to the recombination of localized excitons consists of sharp lines related to individual trapping states. The set of sharp lines is apparently associated with the formation of various oxygen clusters. Therefore, the formation of one sharp line due to excitons bound to 4O10Cd identical clusters in ZnSe-rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Se}_{1-y}$ seems highly probable. The lattice mismatch in ZnSe-rich $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Se}_{1-y}$ is greater than that of ZnS-rich alloys. Accordingly, the 4O10Cd cluster formation in the ZnSe-rich alloys is also more preferred in terms of internal strains. Moreover, the CdSe and ZnO bondings in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Se}_{1-y}$ are less favorable than those of CdS and ZnO in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$. It gives the additional advantage for the 4O10Cd cluster formation in $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Se}_{1-y}$. The contents $y \geq 1 \times 10^{-4}$ and $x \geq 2.5y$ in the last mentioned alloys was considered. The majority of oxygen atoms should be in 4O10Cd clusters over the total temperature range if the alloy contents are $y > 3 \times 10^{-4}$ and $x \approx 2.5y$. The high lattice mismatch ensures the significant cluster formation with the oxygen content in the dilute limit. The temperature dependence of 4O10Cd COPs of the ZnSe-rich alloys with the contents $y = 3 \times 10^{-4}$, 2.25×10^{-4} , 1.5×10^{-4} and $x = 2.5y$ is shown in Fig. 2. The internal strain energy due to compensation may be 3.7 times smaller if almost all oxygen atoms are in 4O10Cd clusters. High-temperature annealing as a cluster formation method can be used for all such alloys. The fulfilled estimates demonstrate that the ZnSe-rich alloys should be semiconductors with 4O10Cd identical clusters

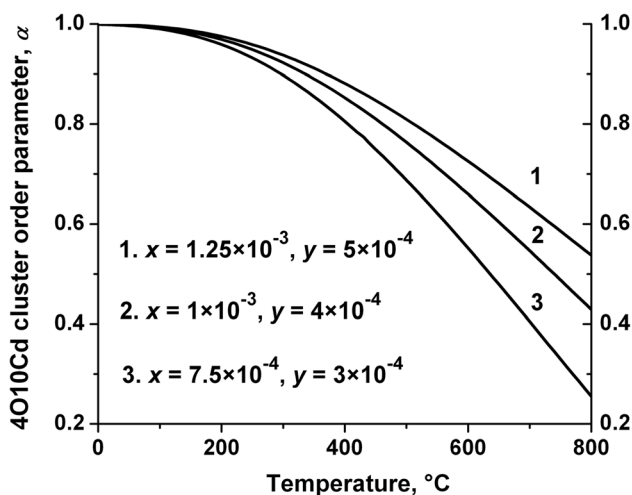


Fig. 1. The temperature dependence of 4O10Cd COPs for $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{S}_{1-y}$ with $y = 5 \times 10^{-4}$, 4×10^{-4} , 3×10^{-4} and $x = 2.5y$

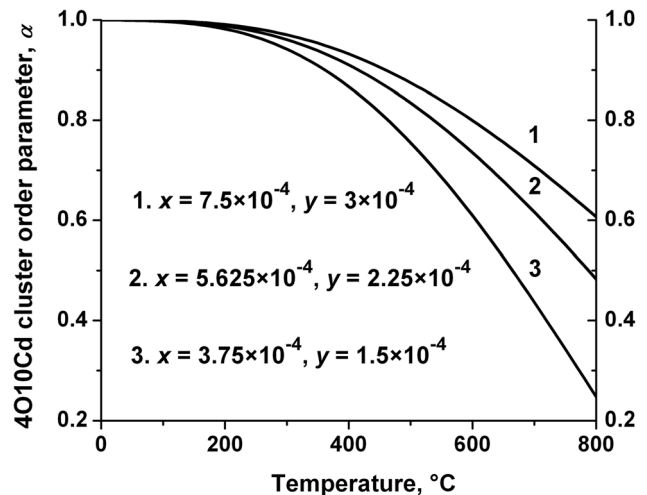


Fig. 2. The temperature dependence of 4O10Cd COPs for $\text{Cd}_x\text{Zn}_{1-x}\text{O}_y\text{Se}_{1-y}$ with $y = 3 \times 10^{-4}$, 2.25×10^{-4} , 1.5×10^{-4} and $x = 2.5y$

in the wide range of the Cd and oxygen contents. Thus, these alloys can be also considered as materials for device applications.

ZnO_yTe_{1-y} films were grown by radical molecular beam epitaxy with the oxygen content up to 1.09%.²³ Such low oxygen content is due to the fact that the lattice mismatch in ZnTe-rich Cd_xZn_{1-x}O_yTe_{1-y} is the largest among the alloys under consideration. Therefore, the internal strain compensation in Cd_xZn_{1-x}O_yTe_{1-y} is the largest despite the fact that the internal strain energy of the alloys with the clusters may be only 1.8 times less than that of the alloys without clusters. The temperature dependence of 4O10Cd COPs for the alloys with $y = 2 \times 10^{-3}$, 1.5×10^{-3} , 1×10^{-3} and $x = 2.5y$ is shown in Fig. 3. The alloys with such contents are suitable if low densities of 4O10Cd clusters are necessary.

The largest compensation of the internal strain energy in Cd_xZn_{1-x}O_ySe_{1-y} after the cluster formation is due to the smallest bond bending elastic constants of CdSe and ZnSe among those of CdB^{VI} and ZnB^{VI} compounds (Table I). The 4O10Cd cluster formation is accompanied mainly by angles between chemical bonds, and the bond bending constants are considerably smaller than the bond stretching constants. Therefore, the deformation energies of angles between bonds play the main role in the compensation of the internal strain energy.

The decrease in the internal strain energy is similar to that in ZnTe-rich Cd_xZn_{1-x}O_yTe_{1-y}, GaAs-rich B_xGa_{1-x}Sb_yAs_{1-y} and InAs-rich B_xIn_{1-x}B_yAs_{1-y} (B^V = Sb, Bi) alloys, respectively, described in.^{7,8,24} 4B10B^V clusters should be formed in InAs-rich B_xIn_{1-x}B_yAs_{1-y}. The decrease in the internal strain energy is also due mainly to the deformation of the angles between bonds. The elastic constants of the angles between bonds are considerably smaller than those of the bonds for A^{III}B^V and A^{II}B^{VI} semiconductors.^{18,20} Thus, the formation of polyatomic identical clusters in which the angles between bonds are

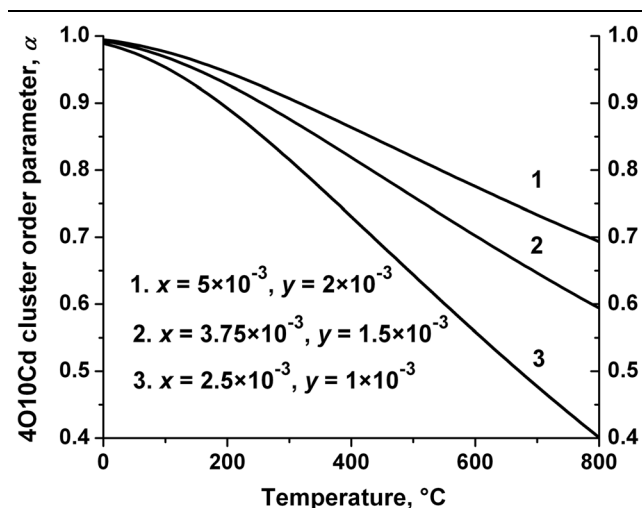


Fig. 3. The temperature dependence of 4O10Cd COPs for Cd_xZn_{1-x}O_yTe_{1-y} with $y = 2 \times 10^{-3}$, 1.5×10^{-3} , 1×10^{-3} and $x = 2.5y$

mainly deformed is a way to transform highly strained, highly mismatched alloys into weakly strained alloys.

CONCLUSION

4O10Cd identical clusters in ZnB^{VI}-rich Cd_xZn_{1-x}O_yB_{1-y}^{VI} (B^{VI} = S, Se, Te) with the Cd and oxygen contents in the dilute limit and more are thermodynamically favorable up to 800°C. Accordingly, such clusters can be formed by using high-temperature annealing if they did not occur during the growth process. The internal strain energies can be reduced up to 2.7, 3.7 and 1.8 times, respectively, after the cluster formation in Cd_xZn_{1-x}O_yS_{1-y}, Cd_xZn_{1-x}O_ySe_{1-y} and Cd_xZn_{1-x}O_yTe_{1-y} if almost all mismatched atoms are in 4O10Cd clusters. The main result of this study is the obtained formation conditions of 4O10Cd identical clusters containing the oxygen tetrahedrons.

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