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Self-assembling of In and nitrogen in GaP:(In, N)



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ABSTRACT

Highly mismatched GaP:N attracts now considerable interest in fabricating ensembles of single photon sources. Significant reduction of undesirable internal strains around nitrogen atoms can be achieved by additional doping with In due to self-assembling of 4N10In and 1N4In clusters in GaP:(In, N). Double doping transforms GaP into GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ substitutional alloy of InN, InP, GaN and GaP. Self-assembling of clusters results in the decrease of the sum of the free energies of the constituent compounds and strain energy. The self-assembling conditions are considered from 0 °C to 1000 °C in the dilute and ultra dilute limits for In and nitrogen impurities, respectively. Almost all nitrogen atoms are in 4N10In clusters over the entire temperature range if $x = 1 \times 10^{-3}$, $y = 1 \times 10^{-4}$; $x = 1 \times 10^{-4}$, $y = 1 \times 10^{-5}$ and $x = 1 \times 10^{-5}$, $y = 1 \times 10^{-6}$. Both types of clusters with considerable densities are in GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ if the ratio between the In and nitrogen contents is 100. If this ratio is ≈ 1000 then all nitrogen impurities are in 1N4In clusters over the entire temperature range. The fulfilled estimates demonstrate that GaP:(In, N) is a promising candidate to fabricate ensembles of single photon sources due to small strains around nitrogen atoms in 4N10In and 1N4In clusters.

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1. Introduction

Ensembles of single photon sources with high optical homogeneity are strongly required to fabricate quantum computers which should considerably improve computational power [1]. In the last few years, GaP:N is studied as one of the semiconductors suitable for such ensembles formation [2,3].

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Isolated nitrogen atoms and nitrogen dyads bound excitons in GaP:N as it was established in the middle of 1960s [4,5]. Isolated nitrogen atoms form very shallow exciton traps in this semiconductor but the dyads result in deep exciton traps with the binding energy that increases with a decrease of the separation between impurities. Moreover, the nitrogen triads also form exciton traps in this material that are significantly deeper than those formed by isolated nitrogen impurities [6].

Nitrogen is a highly mismatched isoelectronic impurity in GaP. However, in spite of this, GaP:N is GaP-rich $\text{GaN}_y\text{P}_{1-y}$ substitutional alloy. Due to the high mismatch the nitrogen concentrations in GaP:N should be significant in order to obtain desired density of nitrogen dyads and triads. Therefore, the δ -doping providing considerable nitrogen concentration as well as significant internal strains in a thin layer is used in the epitaxial growth of GaP:N [2,3]. These strains cause an inadmissible inhomogeneity in the emission energy of the excitons bound to the impurity complexes. That is why, a search of the ways to create the GaP-rich semiconductors with exciton traps lying in the reduced strain fields is important to produce ensembles of the identical single photon sources.

Self-assembling (SA) of identical isoelectronic impurity clusters can be one of the ways to resolve this problem. It was found that SA of 4B10Sb and 1B4Sb clusters reduces considerably the internal strains in GaP:(B, Sb) [7]. 4B10Sb clusters are empty boron tetrahedrons surrounded by Sb impurities and boron atoms in 1B4Sb clusters are in the centers of Sb tetrahedrons. SA of such clusters compensates considerably the dilation and shrinking of the crystal lattice due to isolated boron and Sb atoms, respectively. The reduction of the internal strain energy is one of the reasons of SA. Moreover, double doping with boron and Sb transforms GaP into GaP-rich $\text{B}_x\text{Ga}_{1-x}\text{Sb}_y\text{P}_{1-y}$ substitutional alloy of BSb, BP, GaSb and GaP. An exchange of lattice sites between cations or anions in this alloy leads to the reaction between bonds: $n\text{B-Sb} + n\text{Ga-P} \rightarrow n\text{B-P} + n\text{Ga-Sb}$, ($n = 1, \dots, z$) or vice versa, where z is the co-ordination number. BSb and GaP bonding is thermodynamically preferable over that of BP and GaSb. SA of 4B10Sb and 1B4Sb clusters increases B-Sb and Ga-P bond concentrations and decreases B-P and Ga-Sb bond concentrations. Thus, the increase of the quantities of B-Sb and Ga-P bonds is the second reason of SA.

Similarly, double doping with In and nitrogen transforms GaP into GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ substitutional alloy of InN, InP, GaN and GaP. Isolated In and nitrogen impurities, consequently, shrink and dilate the crystal lattice of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$. SA of 4N10In and 1N4In clusters in GaP:(In, N) as well as SA of 4B10Sb and 1B4Sb clusters in GaP:(B, Sb) should decrease the internal strain energy due to the compensation of the shrinking and dilation since the covalent radii of In and nitrogen are larger and smaller than those of Ga and phosphorus, correspondingly. Moreover, InN and GaP bonding is thermodynamically preferable over that of InP and GaN. Thus, in GaP:(In, N) there are also two causes for SA of 4N10In and 1N4In clusters. The SA conditions of In and nitrogen in GaP:(In, N) are studied here.

2. Theory

4N10In and 1N4In clusters shown in Figs. 1 and 2, correspondingly, should occur in GaP:(In, N) if SA decreases the Helmholtz free energy. The free energy of GaP co-doped with In and nitrogen or GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ substitutional alloy is a sum of three items $g = g^0 + u - Ts$, where g^0 is a sum of the free energies of constituent compounds InN, InP, GaN and GaP, u is the strain energy and $-Ts$ is the configurational entropy term. The 4N10In and 1N4In clustering degrees are represented by 4N10In cluster order parameter (4N10In COP) α and 1N4In cluster order parameter (1N4In COP) β . The parameters are ratios between the numbers of nitrogen atoms in 4N10In and 1N4In clusters and total number of nitrogen atoms.

The sum of the free energies of the constituent compounds is

$$g^0 = \Delta\mu^0(\alpha + \beta)(1 - x)y + \Delta\mu^0xy + \mu_{\text{GaP}}^0 + (\mu_{\text{InP}}^0 - \mu_{\text{GaP}}^0)x + (\mu_{\text{GaN}}^0 - \mu_{\text{GaP}}^0)y, \quad (1)$$

where $\Delta\mu^0 = \mu_{\text{InN}}^0 - \mu_{\text{InP}}^0 - \mu_{\text{GaN}}^0 + \mu_{\text{GaP}}^0$ and μ_{InN}^0 is the free energy of InN. The change of the sum (1) under variations of 4N10In and 1N4In COPs depends only on the first item. Therefore, only it will be taken into account later on. The relation between the free energies is given by

$$\Delta\mu^0 = \Delta h^0 - T\Delta s,$$

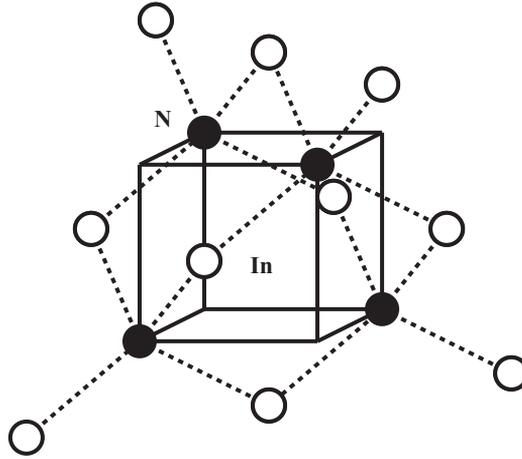


Fig. 1. 4N10In cluster.

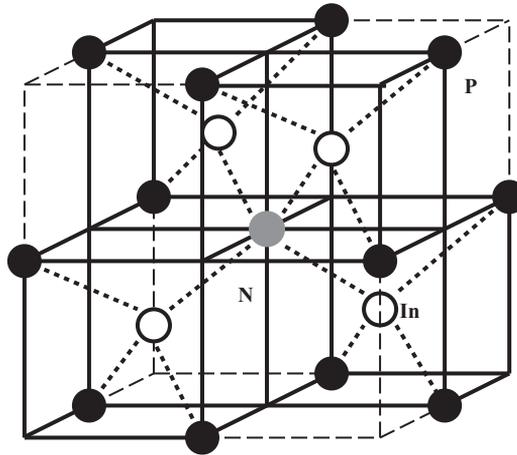


Fig. 2. 1N4In cluster in GaP-rich matrix.

where $\Delta h^0 = h_{\text{InN}} - h_{\text{InP}} - h_{\text{GaN}} + h_{\text{GaP}}$, $\Delta S = S_{\text{InN}} - S_{\text{InP}} - S_{\text{GaN}} + S_{\text{GaP}}$, h_{InN} and S_{InN} are the enthalpy and entropy of InN, respectively. The value of the relation $\Delta h^0 = h_{\text{InN}} - h_{\text{InP}} - h_{\text{GaN}} + h_{\text{GaP}}$ is equal to the value of the relation $\Delta h^f = h_{\text{InN}}^f - h_{\text{InP}}^f - h_{\text{GaN}}^f + h_{\text{GaP}}^f$, where h_{InN}^f is the enthalpy of formation of InN. The relation between the enthalpies of formation is

$$\Delta h^f = \Delta h^{of} + \int_{298.15}^T \Delta c_p dT,$$

where $\Delta h^{of} = h_{\text{InN}}^{of} - h_{\text{InP}}^{of} - h_{\text{GaN}}^{of} + h_{\text{GaP}}^{of}$, h_{InN}^{of} is the standard enthalpy of formation of InN, $\Delta c_p = c_p^{\text{InN}} - c_p^{\text{InP}} - c_p^{\text{GaN}} + c_p^{\text{GaP}}$ and c_p^{InN} is the heat capacity of InN. The relation between the entropies is estimated as

$$\Delta S = \Delta S^0 + \int_{298.15}^T \frac{\Delta c_p}{T} dT,$$

where $\Delta s^0 = s_{\text{InN}}^0 - s_{\text{InP}}^0 - s_{\text{GaN}}^0 + s_{\text{GaP}}^0$ and s_{InN}^0 is the standard entropy of InN. The standard enthalpies of formation and standard entropies as well as the heat capacities of the constituent compounds are available [8].

The strain energy of GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ is

$$u = (1 - \alpha - \beta)yu_{\text{N}} + (x - 2.5\alpha y - 4\beta y)u_{\text{In}} + 0.25\alpha yu_{4\text{N}10\text{In}} + \beta yu_{1\text{N}4\text{In}},$$

where u_{In} , u_{N} , $u_{4\text{N}10\text{In}}$ and $u_{1\text{N}4\text{In}}$ are the strain energies due to isolated In and nitrogen impurities and 4N10In and 1N4In clusters, correspondingly. The strain energies due to both isolated impurities and 1N4In clusters were estimated as sums of two items. The first item is the strain energy of the quadruples of tetrahedral cells situated around isolated In and nitrogen impurities or central atoms of 1N4In clusters. The quadruple of 1N3Ga1In tetrahedral cells or 1N4In cluster surrounded by Ga atoms is shown in Fig. 2. This part of the sums was described by using the valence force field model and by the approach developed for the estimates of the strain energy of III–V ternary alloys [9,10]. The elastic constants of bonds and angles between bonds of the constituent compounds are available [9,11]. The other contribution of the sums is the deformation energy of GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ outside the quadruples. This part was considered as the energy of the elastic media with radial displacements inversely proportional to the square of a distance from the central atoms of the quadruples. The strain energies due to isolated In and nitrogen atoms and 1N4In clusters are equal, respectively, to $u_{\text{In}} = 13.657$ kJ/mol, $u_{\text{N}} = 97.697$ kJ/mol and $u_{1\text{N}4\text{In}} = 43.718$ kJ/mol. These energies demonstrate that SA of 1N4In clusters decreases the strain energy four times due to compensation of the shrinking and dilation of the crystal lattice produced by isolated impurities. Thus, SA of 1N4In clusters is preferable from the strain energy standpoint. The strain energy produced by 4N10In clusters $u_{4\text{N}10\text{In}} = 82.497$ kJ/mol was obtained as the deformation energy of such clusters in the unstrained GaP-rich matrix to reduce the number of unknown variables in the calculations. Therefore, the strained energy should be overestimated. However, even the overestimated value of the energy demonstrates more than six times decrease of the strain energy after SA of 4N10In clusters. The strain energy due to 4N10In clusters was estimated also in the framework of the valence force field model [9] as a sum of the deformation energies of 40 bonds and 144 angles between bonds. The elastic constants of bonds are much larger than those of angles between bonds. Therefore, deformations of angles between bonds are preferable in these clusters. The deformation energy of the angles between bonds is more than 80% of the total strain energy produced by 4N10In clusters. Whereas the deformation energies of angles between bonds due to 1N4In clusters and isolated impurities are $\approx 40\%$ of the total strain energies. SA of 4N10In clusters decreases the strain energies more considerably than SA of the smaller clusters since angles between bonds are mainly distorted in the larger clusters. The deformation energies due to the isolated impurities and clusters were obtained by minimizing the strain energy.

The configurational entropy term is written as

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

The entropy was obtained as a function of the number of different configurations. This number is represented as a product of two factors. The first factor is a number of permutations of atoms when isolated impurities and 1N4In clusters are distributed at random at a fixed location of 4N10In clusters. The second factor is a number of the arrangements of 4N10In clusters.

SA of both types of clusters decreases the sum of the free energies of the constituent compounds, strain energy and configurational entropy. Therefore, SA of 4N10In clusters and SA of 1N4In clusters are competing processes.

3. Results and discussion

$\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys are successfully grown by the different epitaxial methods over the entire composition range. GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ with nitrogen in the ultra dilute limit are considered here

since, in such a case, clusters of both types should be isolated objects and can form localized states. The compositions of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ are chosen from $x = 1 \times 10^{-6}$ to $x = 0.01$ and from $y = 1 \times 10^{-7}$ to $y = 1 \times 10^{-4}$. If the alloys are grown by metalorganic vapor phase epitaxy by using phosphine as a phosphorus precursor then the growth temperatures should be $\approx 900^\circ\text{C}$ and higher to obtain the sufficient decomposition of phosphine. Therefore, the temperature range from 0°C to 1000°C was chosen for the estimates. Moreover, a thermal annealing may be a necessary treatment to reach the equilibrium distribution of atoms if the alloys were grown under non-equilibrium conditions.

If the In and nitrogen contents are equal then only 4N10In clusters can form. All or almost all In atoms should be in such clusters over the entire temperature range if the impurity content is $x = y = 1 \times 10^{-4}$. The temperature dependences of 4N10In COP in alloys with In and nitrogen contents $x = y = 1 \times 10^{-5}$, $x = y = 3 \times 10^{-6}$ and $x = y = 1 \times 10^{-6}$ are shown in Fig. 3. These results demonstrate the considerable increase of 4N10In COP with an increase of the impurity content. The complete or almost complete 4N10In clustering (all or almost all In atoms are in these clusters) is reached at temperatures of $760\text{--}780^\circ\text{C}$, $680\text{--}700^\circ\text{C}$ and $600\text{--}620^\circ\text{C}$ in alloys with $x = y = 1 \times 10^{-5}$, $x = y = 3 \times 10^{-6}$ and $x = y = 1 \times 10^{-6}$, respectively. Thus, the desired density of 4N10In clusters can be obtained at high temperatures. Accordingly, a thermal annealing can be used for the redistribution of In and nitrogen atoms if the clusters do not form in the growth process. The strains around nitrogen atoms in 4N10In clusters in GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ are considerably smaller than those around isolated nitrogen atoms in GaP:N. In 4N10In clusters 12 In–N bonds are stretched only for 1.02% and other 4 In–N bonds are extended for 1.59%, but Ga–N bonds around isolated nitrogen impurities are extended for 4.12% in GaP:N. Accordingly, the formation of excitons bound to 4N10In clusters should be highly probable. Moreover, 4N10In clusters are in an insignificant external strain field due to the ultra dilute limit for nitrogen in comparison with a strain field around nitrogen dyads and triads formed in GaP by using the δ -doping with nitrogen.

Almost all nitrogen atoms are in 4N10In clusters over the entire temperature range if the impurity contents are $x = 10y = 1 \times 10^{-3}$, $x = 10y = 1 \times 10^{-4}$ and $x = 10y = 1 \times 10^{-5}$. Other nitrogen atoms should be in 1N4In clusters. The small density of 1N4In clusters is due to the significant decrease of the configurational entropy at such ratio of the impurity contents. Both types of the clusters have considerable densities if the ratio between the In and nitrogen contents is 100. The temperature dependences of 4N10In and 1N4In COPs in $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ with impurity contents $x = 1 \times 10^{-2}$, $y = 1 \times 10^{-4}$; $x = 1 \times 10^{-3}$, $y = 1 \times 10^{-5}$ and $x = 1 \times 10^{-4}$, $y = 1 \times 10^{-6}$ are shown in Fig. 4. If large densities of both type clusters are desirable then $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ should be grown with such impurity contents. Grown $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ will be in the “frozen” state at RT since the transformation of 1N4In into 4N10In clusters is hardly probable due to the low self-diffusion rates and the ultra dilute limit for nitrogen. If the ratio between the In and nitrogen contents is ≈ 1000 then all nitrogen atoms are in 1N4In clusters over the entire temperature range. It is due to the insignificant decrease of the configurational entropy after

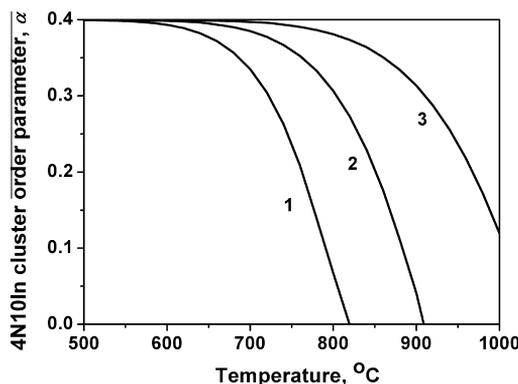


Fig. 3. The temperature dependencies of the 4N10In cluster order parameters. The curves 1, 2 and 3 correspond to compositions $x = y = 1 \times 10^{-6}$, $x = y = 3 \times 10^{-6}$ and $x = y = 1 \times 10^{-5}$, respectively.

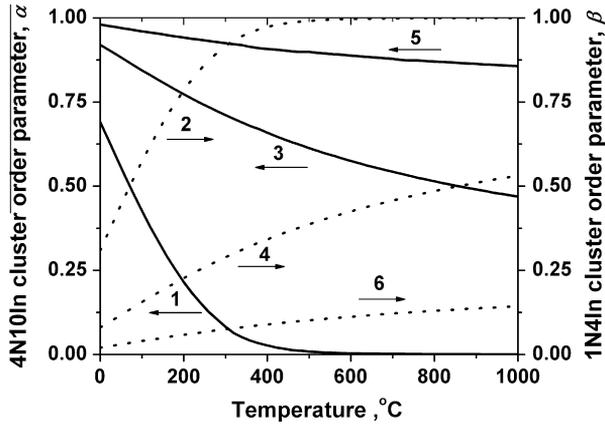


Fig. 4. The temperature dependencies of the 4N10In (solid curves 1, 3 and 5) and 1N4In (dotted curves 2, 4 and 6) cluster order parameters. The curves 1, 3, 5 and curves 2, 4, 6 correspond to compositions $x = 1 \times 10^{-2}, y = 1 \times 10^{-4}$; $x = 1 \times 10^{-3}, y = 1 \times 10^{-5}$ and $x = 1 \times 10^{-4}, y = 1 \times 10^{-6}$, correspondingly.

SA of such clusters. 1N4In clusters may also be attractive from the formation of localized excitons standpoint since nitrogen atoms in such clusters are in the almost unstrained state in comparison with isolated nitrogen atoms in GaP:N. In–N bonds in 1N4In clusters in GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ are stretched only for 0.37% due to compensation of the strains and Ga–N bonds in GaP:N are extended for 4.12% as it was mentioned above. Accordingly, the strain energy of In–N bond in 1N4In clusters should be more than a hundred times smaller than that of Ga–N bond in GaP:N. As it was shown [12], the extension of Ga–N bonds is the cause of the small binding energy of excitons bound to isolated nitrogen atoms in GaP:N. Therefore, the significant decrease of the strains around nitrogen atoms after SA of 1N4In clusters should lead to a considerable increase of the binding energy. To obtain the large binding energy of excitons the δ -doping with nitrogen is used [2]. In such a case, excitons are bound to the nitrogen dyads and triads. SA of 1N4In clusters in GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ with nitrogen in the ultra dilute limit represented in this study can be the alternative to the δ -doping with nitrogen of GaP. SA of 1N4In clusters has an advantage in comparison with the δ -doping of GaP since nitrogen complexes are in the significant random internal strain field. Accordingly, excitons bound to the nitrogen complexes should have an undesirable inhomogeneity of the emission energy. In GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ with nitrogen in the ultra dilute limit, 1N4In clusters are in the random internal strain field due to isolated In atoms. However, the strains caused by In atoms are considerably smaller than those due to nitrogen atoms since $\text{In}_x\text{Ga}_{1-x}\text{P}$ are less mismatched alloys than $\text{GaN}_y\text{P}_{1-y}$.

The represented SA conditions demonstrate that GaP:(In, N) can be formed with 4N10In or 1N4In clusters as well as with the clusters of both types. In addition, the desired densities of the clusters can be obtained under these conditions.

4. Conclusions

To conclude, GaP co-doped with In and nitrogen is GaP-rich $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ alloy in which self-assembling of 4N10In and 1N4In clusters should be in the wide temperature and impurity content ranges. The type and content of the clusters depend on the temperature and impurity contents. The preferential InN and GaP bonding over that of InP and GaN and considerable compensation of the internal strains are causes of self-assembling. 4N10In and 1N4In clusters should be in the insignificant strain field since at least the majority of nitrogen atoms are in the clusters. Accordingly, the formation of excitons bound to 4N10In and 1N4In clusters is highly probable. Thus, GaP:(In, N) is a promising candidate to fabricate ensembles of the identical single photon sources.

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References

- [1] S. Reitzenstein, *IEEE J. Select Topics Quantum Electron.* 18 (2012) 1733–1746.
- [2] P. St-Jean, G. Éthier-Majcher, Y. Sakuma, S. Francoeur, *Phys. Rev. B* 89 (2014) 075308.
- [3] M. Ikezawa, Y. Sakuma, Y. Masumoto, *Jpn. J. Appl. Phys.* 36 (2007) L871–L873.
- [4] D.G. Thomas, J.J. Hopfield, C.J. Frosch, *Phys. Rev. Lett.* 15 (1965) 857–860.
- [5] D.G. Thomas, J.J. Hopfield, *Phys. Rev.* 150 (1966) 680–689.
- [6] B. Gil, H. Mariete, *Phys. Rev. B* 35 (1987) 7999–8004.
- [7] V.A. Elyukhin, *Superlattices Microstruct.* 60 (2013) 320–326.
- [8] Landolt-Börnstein, *Numerical Data and Functional Relations in Science and Technology, New Series*, in: M. Shulz, H. Weiss (Eds.), 17d, Springer, Berlin, 1984, p. 16.
- [9] R.M. Martin, *Phys. Rev. B* 1 (1970) 4005–4011.
- [10] V.A. Elyukhin, L.P. Sorokina, *Sov. Phys. Dokl.* 31 (1986) 342–344.
- [11] V.A. Elyukhin, S.A. Nikishin, *Semicond. Sci. Technol.* 11 (1996) 917–920.
- [12] J.C. Phillips, *Phys. Rev. Lett.* 22 (1969) 285–287.