Vacancy-migration-mediated disordering in CuPt-ordered (Ga,In)P studied by *in situ* optical spectroscopy in a transmission electron microscope

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(Received 2 June 1998)

We examined electron-irradiation-induced disordering in CuPt-ordered (Ga,In)P by *in situ* photoluminescence and cathodoluminescence spectroscopy in a transmission electron microscope. A decrease of luminescence intensity following an electron irradiation in the energy range above 120 keV has been observed. We have shown that the decrease is due to the Frenkel-type defects on the Ga and In sublattices generated by electron irradiation, and the threshold electron energies for the displacement of Ga and In atoms have been estimated to be 145 and 120 keV, respectively. We propose that (1) electron-irradiation-induced migration of group-III (Ga and In) vacancies dominates the disordering in the dose range below $2\times10^{20}\,\mathrm{cm}^{-2}$, and (2) spontaneous recombination of group-III vacancies and interstitials dominates the disordering in the dose range above $5\times10^{21}\,\mathrm{cm}^{-2}$. [S0163-1829(99)03904-1]

I. INTRODUCTION

Fundamental defect reactions in semiconductors such as the generation and migration of point defects have been intensively examined, since these reactions strongly affect the optical and electronic properties of final products. For studying the reactions, electron irradiation is often used to produce pairs of an isolated interstitial and a vacancy (i.e., Frenkel pairs) in a crystal. In III-V compound semiconductors, antisites as well as Frenkel pairs are introduced simultaneously by this method. Moreover, some defects in III-V compounds anneal during electron irradiation due to ionization-induced migration. Because of these complications, there are still many open questions concerning defect reactions in III-V compounds.

The generation processes of electron-irradiation-induced defects have been widely studied by deep level transient spectroscopy (DLTS). Several irradiation-induced traps have been found in GaAs,[1] InP,[2] GaP,[3] and other III-V compound semiconductors (Ref. 4). In InP, by measuring the electron-energy dependence of the introduction rates of the H4 and H5 traps, the energy levels at $E_v-0.37$ and $E_v-0.53$ eV, respectively, the threshold electron energies for the displacement of In and P atoms have been evaluated separately (about 120–170 and 100 keV).[5] In other III-V compounds, the energies to create defects have been estimated, but the energy values are not assigned to the sublattices. The explanation is that the generation rates of some irradiation-induced defects are affected by ionization-induced migration (Ref. 4). However, other experiments will be required to understand quantitatively the generation process of point defects in III-V compounds.

Owing to the thermal migration of interstitials and vacancies, many irradiation-induced defects disappear during annealing after electron irradiation. The migration processes of defects in GaAs have been well investigated; isolated As vacancies in GaAs are identified by positron annihilation spectroscopy[6] (PAS) and electron spin resonance,[7] and the As defects anneal at temperatures of about 500 and 723 K. The same annealing stages have also been observed by Huang diffuse scattering[8] (HDS) and DLTS.[9] The former stage is attributed to the recombination of Frenkel pairs at the As sublattice through the migration of isolated As interstitials, and the latter is due to the migration of isolated As vacancies. The migration of isolated Ga interstitials in GaAs presumably causes the annealing stage in a temperature range from 77 to 500 K observed by HDS (Ref. 8) and PAS.[10] The irradiation-induced H2, H3, and H4 traps in InP show similar annealing properties as in GaAs,[11] and the annealing of these traps at around 400 K may be due to the thermal migration of isolated P interstitials. The annealing mechanisms of other defects in III-V compounds are still debatable.

As mentioned above, the generation and migration processes of defects in III-V compound semiconductors have not yet been fully clarified. In the present study, we systematically investigated the electron-irradiation-induced disordering in CuPt-ordered (Ga,In)P that is caused by the migration of group-III (Ga and In) interstitials and vacancies generated by electron irradiation. The first aim of this article is a detailed study of the kinetics of point-defect reactions under electron irradiation by *in situ* cathodoluminescence (CL) and photoluminescence (PL) spectroscopy in a transmission electron microscope (TEM). We then discuss a disordering model based on electron-irradiation-induced migration of group-III vacancies. The method of *in situ* optical spectroscopy in a TEM,[12] which enables us to observe *in situ* the variation of both the atomic and electronic structures in material under electron irradiation, was first applied to a study of point-defect reactions under electron irradiation.

II. EXPERIMENTS

The CuPt-ordered (Ga,In)P sample was grown on a GaAs substrate by metal-organic vapor-phase epitaxy at 700 °C; the substrate angle was 2° off from (001) towards $[1\bar{1}0]$. Cross sections of the sample for *in situ* CL and PL spectroscopy and electron microscopy were prepared using a conventional etching method with Ar^+ ions. These specimens were then irradiated with an electron beam in a TEM at a tempera-

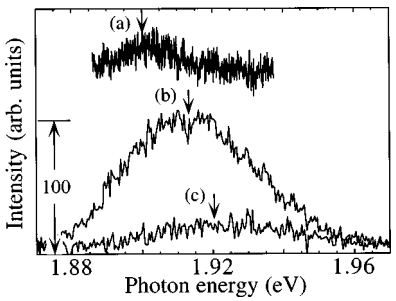

FIG. 1. (a) PL spectrum of an as-grown specimen observed at 20 K. (b) CL spectrum of an as-grown specimen measured at 110 K. The CL peak intensity was normalized to 100. (c) CL spectrum obtained after electron irradiation; the incident-electron energy was 170 keV, and the electron dose was $4.8\times10^{19}\,\mathrm{cm}^{-2}$.

ture of 110 K; the direction of the incident beam was kept parallel to the [110] zone axis. The incident electron energy E ranged from 100 to 170 keV, and the electron dose D, i.e., electron flux ϕ ($7.8\times10^{16}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$) multiplied by irradiation time t_{ir}, was up to $1.0\times10^{23}\,\mathrm{cm}^{-2}$. The irradiated areas were about 20 μm in diameter.

The irradiated specimens were characterized by CL and PL spectroscopy. CL and PL emissions from an irradiated area were measured in the TEM immediately after electron irradiation, as described in Ref. 12. Since irradiation by 100-keV electrons did not vary luminescence spectra (Secs. III A and III C 1), a 100-keV electron beam was used for the excitation of CL with flux $\phi=1.2\times10^{16}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ and measurement temperature $T_m=110$ K. PL was excited with the 514.5-nm line of an Ar^+ laser (excitation power of about 2 mW, and $T_m=20$ K). CL was measured in the absence of laser-beam illumination, and the electron beam was switched off during PL measurements. Therefore CL emission did not overlap with PL emission and vice versa. Figures 1(a)–1(c) show examples of PL and CL profiles. The irradiated specimens were also characterized by transmission electron diffraction (TED), as described in Ref. 13.

The degree of atomic ordering in GaInP is characterized by an order parameter S.[14] The relationship between the band-gap energy and S has been discussed theoretically[15,16] and experimentally,[17,18] and S has been evaluated by an equation[17] $S=\{(2.005-E_{\mathrm{PL}(<30\,\mathrm{K})})/0.471\}^{0.5}$ where $E_{\mathrm{PL}(<30\,\mathrm{K})}$ denotes PL peak energy in eV measured below 30 K.[19] From the results of PL and CL measurements for as-grown [Figs. 1(a) and 1(b)] and several electron-irradiated specimens, we determined that the CL peak energy obtained at 110 K, $E_{\mathrm{CL}(110\,\mathrm{K})}$, is given by $E_{\mathrm{CL}(110\,\mathrm{K})}=E_{\mathrm{PL}(<30\,\mathrm{K})}+0.012$ eV. Hence S could be estimated by

$$S=\{(2.017-E_{\mathrm{CL}(110\,\mathrm{K})})/0.471\}^{0.5}. \quad (1)$$

S was also estimated by transmission electron diffraction using a 100-keV electron beam and was approximately given by $S=S_0\{I_{\mathrm{TED}}(D)/I_{\mathrm{TED}}(0)\}^{0.5}$ where S_0 and $I_{\mathrm{TED}}(D)$ denote the order parameter for an as-grown specimen and the dose-dependent TED intensity of an ordered spot, respectively.[13]

III. RESULTS AND DISCUSSION

A. Decrease of order parameter due to electron irradiation

The CL peak energy $E_{\mathrm{CL}(110\,\mathrm{K})}$ of an electron-irradiated specimen shifted to a higher value compared to an as-grown

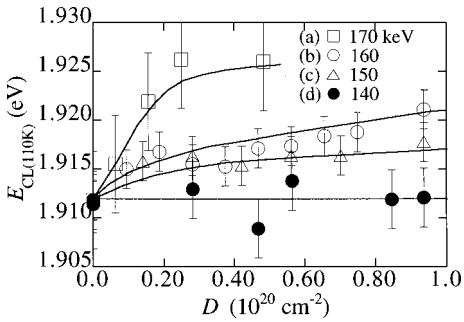

FIG. 2. CL peak energy $E_{\mathrm{CL}(110\,\mathrm{K})}$ vs electron dose D. Incident-electron energies are indicated in the figure.

one [as an example, see Figs. 1(b) and 1(c)]; i.e., S decreased after electron irradiation. $E_{\mathrm{CL}(110\,\mathrm{K})}$ for various D and E were measured [Figs. 2(a)–2(d)], and we obtained the relationships of S with D for several incident-electron energies (Fig. 3). We found that S decreases with increasing D in the range $E>140$ keV [Figs. 3(a)–3(c)]. S was unchanged after electron irradiation when $E\leqslant140$ keV; Fig. 3(d) shows a result at $E=140$ keV.

As shown in Fig. 3, we could obtain a detailed dose dependence of S using optical spectroscopy with an experimental error for S of less than 0.008. The method was, however, applicable only in the dose range $D\leqslant1.5\times10^{20}\,\mathrm{cm}^{-2}$, since CL peak intensity, as well as S, decreased with increasing D [as an example, see Figs. 1(b) and 1(c)]: and no CL emission was detectable when $D>1.5\times10^{20}\,\mathrm{cm}^{-2}$ (Sec. III C 1). We unavoidably supplemented the dose dependence of S by a TED method (Fig. 4), even though the experimental error for S (about 0.018) was rather large. We found that S decreases gradually with increasing D when $E>140$ keV [Figs. 4(a)–4(c)]; two disordering stages in the dose ranges $D<2\times10^{20}\,\mathrm{cm}^{-2}$ and $D>5\times10^{21}\,\mathrm{cm}^{-2}$ were clearly observable. In the latter stage, S decreased exponentially with increasing D with a decay rate μ: $\mu=(1.5\pm0.5)\times10^{-24}$ (150 keV), $(7.0\pm1.0)\times10^{-24}$ (160 keV), and $(13.0\pm2.0)\times10^{-24}\,\mathrm{cm}^2$ (170 keV), respectively.

B. Disordering process in the dose range $D>5\times10^{21}\,\mathrm{cm}^{-2}$

As shown in the preceding section, we found the existence of two disordering stages in the dose ranges $D<2\times10^{20}\,\mathrm{cm}^{-2}$ and $D>5\times10^{21}\,\mathrm{cm}^{-2}$. The order-disorder reac-

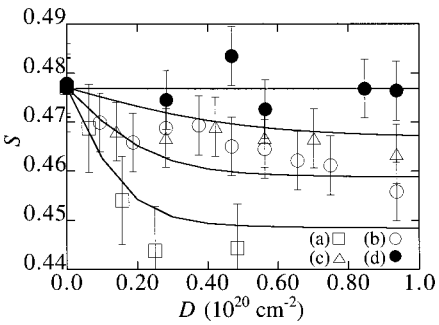

FIG. 3. Order parameter S estimated by optical spectroscopy vs electron dose D. Symbols have the same meaning as in Fig. 2. Curves denote the theoretical calculations from Eq. (9) ($K_{(\mathrm{Ga})}=K_{(\mathrm{In})}=7$ and $K_{IV(\mathrm{Ga})}=K_{IV(\mathrm{In})}=0.2$).

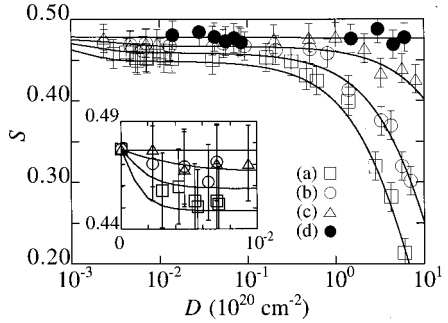

FIG. 4. Order parameter S estimated by TED method vs electron dose D. Symbols have the same meaning as in Fig. 2. Curves denote the theoretical calculations from Eq. (9) ($K_{(\mathrm{Ga})}=K_{(\mathrm{In})}=7$ and $K_{IV(\mathrm{Ga})}=K_{IV(\mathrm{In})}=0.2$).

tion under electron irradiation is generally explained by three kinds of effects:[22] the change of S with respect to irradiation time can be expressed by an equation $dS/dt_{\mathrm{ir}}=[dS/dt_{\mathrm{ir}}]_{\mathrm{spon}}+[dS/dt_{\mathrm{ir}}]_{\mathrm{se}}+[dS/dt_{\mathrm{ir}}]_{\mathrm{va}}$, where the first, second, and third terms represent the change of S owing to spontaneous recombinations of an interstitial and a vacancy, sequential collisions, and vacancy migrations, respectively. The latter stage has been examined and the disordering is attributed to spontaneous recombinations of a group-III (Ga and In) interstitial and a vacancy generated by electron irradiation.[13] Before we discuss the newly observed former stage, let us recall the analytical results obtained from the spontaneous recombination model.[13]

(1) Each concentration of primary defects (isolated vacancies, isolated interstitials, and pairs of an isolated vacancy and an interstitial) comes to a steady-state value immediately after irradiation commences.

(2) Under steady-state conditions the change of S is expressed by

$$\left[\frac{dS}{dt_{\mathrm{ir}}}\right]_{\mathrm{spon}}=-\frac{\sigma_{(\mathrm{Ga})}\sigma_{(\mathrm{In})}}{\sigma_{(\mathrm{Ga})}+\sigma_{(\mathrm{In})}}(1-f)\phi S, \tag{2}$$

and thus

$$\ln\left[\frac{S}{S_0}\right]=-\frac{\sigma_{(\mathrm{Ga})}\sigma_{(\mathrm{In})}}{\sigma_{(\mathrm{Ga})}+\sigma_{(\mathrm{In})}}(1-f)D, \tag{3}$$

in which f represents the correlated recombination factor, $\sigma_{(\mathrm{Ga})}$ and $\sigma_{(\mathrm{In})}$ the cross sections for displacement damage of Ga and In atoms, respectively; S decreases exponentially with increasing D with the decay rate of $\sigma_{(\mathrm{Ga})}\sigma_{(\mathrm{In})}(1-f)/\{\sigma_{(\mathrm{Ga})}+\sigma_{(\mathrm{In})}\}$.

(3) The threshold electron energies for the displacement of Ga and In atoms $E_{d(\mathrm{Ga})}$ and $E_{d(\mathrm{In})}$ are estimated as in the range between 120 and 150 keV. We have confirmed that Eq. (3) expresses the dose dependence of S in the range $D>5\times10^{21}\,\mathrm{cm}^{-2}$ well: the value of μ corresponds to $\sigma_{(\mathrm{Ga})}\sigma_{(\mathrm{In})}(1-f)/\{\sigma_{(\mathrm{Ga})}+\sigma_{(\mathrm{In})}\}$ under the assumption that $E_{d(\mathrm{Ga})}=147\pm5$ keV and $E_{d(\mathrm{In})}\leqslant E_{d(\mathrm{Ga})}$, respectively.[23]

C. Disordering process in the dose range $D<2\times10^{20}\,\mathrm{cm}^{-2}$

The spontaneous recombination model cannot yield the dose dependence of S in the range $D<2\times10^{20}\,\mathrm{cm}^{-2}$: the order parameter estimated by Eq. (3) is much larger than the

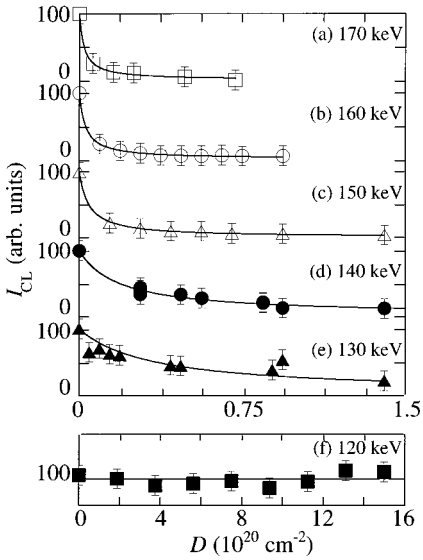

FIG. 5. Normalized CL peak intensity I_{CL} vs electron dose D. Incident-electron energies are denoted in the figure. Each solid line is the best fit of Eq. (4) to the experiments.

experiments. For example, when $E=170$ keV and $D=5.0\times10^{19}\,\mathrm{cm}^{-2}$, the model yields the result that $S=0.477$, which does not correspond to the experimental result of $S=0.445\pm0.008$ [Fig. 3(a)]. The effect of sequential collisions may be disregarded in the present study, i.e., $[dS/dt_{\mathrm{ir}}]_{\mathrm{se}}=0$, since the incident-electron energies used in the experiments were very close to the threshold electron energies for atomic displacements. We therefore considered that the disordering in the range $D<2\times10^{20}\,\mathrm{cm}^{-2}$ is attributed to the migration of vacancies introduced by electron irradiation. So far, there has been little information on the generation and migration of primary defects, including vacancies, in (Ga, In)P under electron irradiation. For a quantitative understanding of the disordering in the range, we discuss the generation process of point defects in detail.

1. Generation of Frenkel-type defects under electron irradiation

The CL peak intensity I_{CL} of an electron-irradiated specimen decreased to a lower value compared to an as-grown one [as an example, see Figs. 1(b) and 1(c)]. We found that I_{CL} was well expressed by a function

$$I_{\mathrm{CL}}=\frac{100}{1+\sigma_1 D}, \tag{4}$$

where σ_1 is a fit parameter; Figs. 5(a)–5(f) show experimental (marks) and simulated (solid lines) I_{CL} vs D for several incident-electron energies. We found that the decrease is well explained by a recombination-center model;[24] i.e., some localized energy levels of electron-irradiation-induced defects act as nonradiative recombination centers, and I_{CL} is given by the function

$$I_{\mathrm{CL}}=\frac{100}{1+\sum_i \sigma_{D(i)}\nu C_{(i)}/\{\tau_r^{-1}+\tau_{\mathrm{nr}}^{-1}\}}, \tag{5}$$

where $C_{(i)}$ represents the concentration of the ith nonradiative center. $\sigma_{D(i)}$ is the capture cross section for carriers (electrons and holes) becoming trapped in the ith center, and ν the velocity of carriers; τ_r and $\tau_{\rm nr}$ denote the carrier lifetimes for the radiative recombination and for nonradiative recombination due to electron-phonon interactions, respectively. $\sigma_{D(i)}\nu/\{\tau_r^{-1}+\tau_{\rm nr}^{-1}\}$ may remain constant during the present CL measurements. Comparing the experimental result given by Eq. (4) with the theoretical one from Eq. (5), we conclude that $C_{(i)}$ increases linearly with increasing D, i.e., $C_{(i)}=\alpha_{(i)}D$ in which $\alpha_{(i)}$ represents the introduction rate for the ith nonradiative center. This indicates that the nonradiative centers are related to primary defects generated by electron irradiation.

We next discuss the nature of the above-mentioned nonradiative centers. No active energy level in the band gap due to isolated interstitials has been detected to our knowledge, implying that the interstitials are irrelevant to the centers. Since the threshold electron energy for the displacement of P atoms is experimentally suggested to be 100 keV,[13] we deduce that the centers are not related to P vacancies. So far, Frenkel-type defects have been observed in electron-irradiated GaInP,[25] even though the atomic configurations of the defects are still uncertain. It is generally believed that Frenkel-type defects in semiconductors form localized energy levels in the band gap and some of the levels act as recombination centers. We therefore consider that Frenkel-type defects on the Ga and In sublattices are related to the nonradiative centers. The change of the concentration of each defect with respect to irradiation time is theoretically predicted by the equation[26]

$$\frac{dC_{IV(\xi)}}{dt_{\rm ir}}=\sigma_{(\xi)}(1-f)\phi-K_{IV(\xi)}C_{IV(\xi)}^2, \tag{6}$$

where $C_{IV(\xi)}$ represents the concentration of the Frenkel-type defects on the ξ sublattice (pairs of an isolated ξ interstitial and a ξ vacancy, ξ=Ga and In). $K_{IV(\xi)}$ is proportional to the sum of the mobility of the ξ interstitials and that of vacancies on the ξ sublattice. Numerical calculations of Eq. (6) provide the result that $C_{IV(\xi)}$ approximates to $\sigma_{(\xi)}(1-f)D$ for $D<\{\phi/\sigma_{(\xi)}(1-f)K_{IV(\xi)}\}^{0.5}$ (in the order of $10^{20}\,{\rm cm}^{-2}$). In the case where all defects act as nonradiative recombination centers, σ_1 is

$$\sigma_1=\frac{\nu(1-f)\sum_{\xi}\sigma_D(\xi)\sigma_{(\xi)}}{\{\tau_r^{-1}+\tau_{\rm nr}^{-1}\}}. \tag{7}$$

The electron-energy dependence of σ_1 (closed circles in Fig. 6) was well expressed by the theoretical equation when $E_{d(\rm Ga)}=143\pm5$ keV and $E_{d(\rm In)}=120\pm2$ keV, respectively; the solid line in Fig. 6 shows the best fit of Eq. (7) to the experiments. We thus conclude that $I_{\rm CL}$ decreased owing to the Frenkel-type defects on the Ga and In sublattices generated by electron irradiation.

From the results in this section and in Sec. III B, we can estimate $E_{d(\rm Ga)}$ and $E_{d(\rm In)}$ to be 145 ± 2 and 120 ± 2 keV, respectively. This conclusion is consistent with the result in Ref. 13.

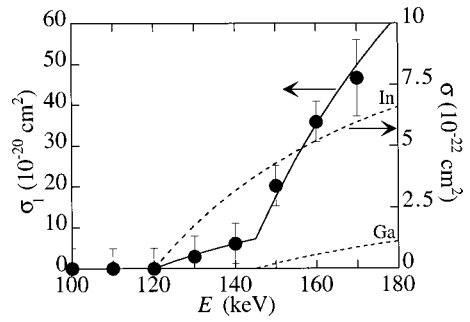

FIG. 6. Fitting parameter σ_1 for the fits indicated in Fig. 5 vs incident-electron energy E. Broken lines represent the theoretical cross sections for displacement damage of the Ga and In atoms, $\sigma_{(\rm Ga)}$ and $\sigma_{(\rm In)}$ vs E ($E_{d(\rm Ga)}=143$ keV, $E_{d(\rm In)}=120$ keV). The solid line is a fit of Eq. (5) to the data.

2. Vacancy-migration-mediated disordering under electron irradiation

We now return to the disordering process in the range $D<2\times10^{20}\,{\rm cm}^{-2}$. Before we discuss the results in this dose range, let us recall briefly a standard model of vacancy-migration-induced disordering: $[dS/dt_{\rm ir}]_{\rm va}\propto-\Sigma_\xi C_{V(\xi)}S$ in which $C_{V(\xi)}$ represents the concentration of the ξ vacancy. This model describes the disordering in ion-implanted (Ga, In)P well.[27]

The above-mentioned model is insufficient to explain the present experiments; an analysis based on the model yields the result that S decreases monotonously with increasing D. We propose an extended vacancy-migration model in which the change of S is related to the concentration gradient, as well as the concentration, of the ξ vacancy; the disordering can be expressed by an equation

$$\left[\frac{\partial S}{\partial t_{\rm ir}}\right]_{\rm va}=-\sum_{\xi}\{\alpha_{(\xi)}\nabla^2+\beta_{(\xi)}\}D_{V(\xi)}C_{V(\xi)}S, \tag{8}$$

in which $D_{V(\xi)}$ represents the diffusion constant of the ξ vacancy under electron irradiation, and $\alpha_{(\xi)}$ and $\beta_{(\xi)}$ are disordering efficiency factors. As we discuss in the following section, a recombination-enhanced effect may promote the motion of the vacancies under electron irradiation. However, since the irradiation temperature (110 K) was very low, the value of $D_{V(\xi)}$ must be small during the present experiments. We therefore consider that the value of the second term in Eq. (8) can be negligible. Assuming $\nabla^2 D_{V(\xi)}C_{V(\xi)}$ is in proportion to the differential of $C_{V(\xi)}$ with respect to $t_{\rm ir}$, $[dS/dt_{\rm ir}]_{\rm va}$ may be proportional to $dC_{IV(\xi)}/dt_{\rm ir}$. Hence the change of S can be expressed by a simple equation

$$\frac{dS}{dt_{\rm ir}}=-\frac{\sigma_{(\rm Ga)}\sigma_{(\rm In)}}{\sigma_{(\rm Ga)}+\sigma_{(\rm In)}}(1-f)\phi S-\sum_{\xi}K_{(\xi)}\frac{dC_{IV(\xi)}}{dt_{\rm ir}}S, \tag{9}$$

where K is a disordering efficiency factor. The phenomenological factor K should be proportional to the number of atomic sites around a vacancy for the migration of the vacancy. Analytical calculation of Eqs. (6) and (9) provides the equation

$$\ln\left[\frac{S}{S_0}\right] = -\frac{\sigma_{(\mathrm{Ga})}\sigma_{(\mathrm{In})}}{\sigma_{(\mathrm{Ga})}+\sigma_{(\mathrm{In})}}(1-f)D - \sum_{\xi} K_{(\xi)} \times \left\{\frac{\sigma_{(\xi)}(1-f)\phi}{K_{IV(\xi)}}\right\}^{0.5} \times \tanh\left[\left\{\frac{\sigma_{(\xi)}(1-f)K_{IV(\xi)}}{\phi}\right\}^{0.5} D\right], \qquad (10)$$

where the second term is related to the disordering by the migration of group-III vacancies under electron irradiation. The dose dependence of S (Figs. 3 and 4) is well expressed by Eq. (10) when the values of K and K_{IV} are on the order of 10^0 and 10^{-1}, respectively; solid lines in the figures show simulated curves of S vs D. For $D>5\times10^{21}\,\mathrm{cm}^{-2}$, the value of the second term comes to a small steady-state value and thus Eq. (10) almost corresponds to Eq. (3). The value of the first term is negligible in the range $D<2\times10^{20}\,\mathrm{cm}^{-2}$, and hence the migration of group-III vacancies under electron irradiation dominates the disordering in this dose range.

As shown in Figs. 3 and 4, all experimental data have been consistently expressed by Eq. (10), and thus we have concluded that group-III vacancies can migrate at a temperature of 110 K under electron irradiation. So far, the migration of these vacancies has been observed only in a temperature range above 923 K.[27] We showed that the CL peak intensity decreases owing to nonradiative electron-hole recombination (Sec. III C 1), and the energy of the recombination may enhance the motion of the group-III vacancies (recombination-enhanced migration). Such a recombination-enhanced effect has been widely investigated in semiconducting materials, since the electronic and optical properties may vary drastically as a result of the effect; as an example, it is considered that dislocation climbs[28] and rapid migrations of impurities[29] due to the effect cause the degradation of some GaAs-based laser diodes. Similar effects have also been observed in Si,[30] GaP,[3] and InP.[31] We could first observe the recombination-enhanced migration of the group-III vacancies in (Ga,In)P, and the present experimental data may be useful for a general understanding of point-defect reactions under electron irradiation.

IV. CONCLUSION

We investigated electron-irradiation-induced disordering of the CuPt-type ordered structure in (Ga,In)P by *in situ* photoluminescence and cathodoluminescence spectroscopy in a transmission electron microscope. A decrease of luminescence intensity following an electron irradiation in the energy range above 120 keV has been observed and we have shown that the decrease is due to Frenkel-type defects on the Ga and In sublattices generated by the irradiation. We conclude that (1) electron-irradiation-induced migration of group-III (Ga and In) vacancies dominates the disordering in the dose range below $2\times10^{20}\,\mathrm{cm}^{-2}$, and (2) spontaneous recombinations of a group-III vacancy and an interstitial dominate the disordering in the dose range above $5\times10^{21}\,\mathrm{cm}^{-2}$. The former conclusion suggests that group-III vacancies can migrate at a temperature of 110 K under electron irradiation due to a recombination-enhanced effect.

This study has provided additional experimental data about the generation and migration of Ga and In vacancies under electron irradiation. The method of *in situ* optical spectroscopy in a TEM is useful for studying defect reactions under electron irradiation.

ACKNOWLEDGMENTS

The (Ga,In)P sample was provided by Mitsubishi Chemical Co. This work was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (C), No. 09640395, 1997–1998, and Grant-in-Aid for Scientific Research on Priority Areas (Phase transformations), No. 09242222, 1997, and No. 10136226, 1998.

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