Photoluminescence Spectroscopy of Localized Excitons in $Si_{1-x}Ge_x$

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We have recently found that high quantum efficiency can be achieved in strained $Si_{1-x}Ge_x$ alloy layers through the elimination of nonradiative channels. We observed a photoluminescence process in SiGe grown on <100> silicon by rapid thermal chemical vapor deposition, which was attributed to free excitons localized by random fluctuations in alloy composition. The external quantum efficiency of this process was measured directly for a single $Si_{0.75}Ge_{0.25}$ quantum well and found to be extraordinarily high, about 11.5 ± 2%. In this paper, we present additional data on the localized exciton photoluminescence, including temperature dependence, time decay curves, and effects of sample annealing.

Key words: Localized excitons, photoluminescence spectroscopy, $Si_{1-x}Ge_x$

INTRODUCTION

In recent years, researchers have shown increasing interest in strained epitaxial layers from the Si-Ge alloy system. This stems partly from the advantages offered by heterostructures in electronic devices. As well, studies have been motivated by the possibility of silicon-based optoelectronics through the quasi-direct band gap predicted to occur by zone-folding in strained atomic layer Si/Ge superlattices.[1,2] While evidence for the direct band gap has remained inconclusive,[3-7] other studies have recently met with some success in understanding the optical properties of the SiGe alloy grown epitaxially on silicon. This is largely due to the observation of band edge photoluminescence (PL) from free excitons or shallow bound excitons, which gives direct information about the epitaxial layer quality, the band gap variation due to alloy composition and strain, and any quantum confinement effects.[8-14]

While such information is invaluable in heterostructure device design, our PL studies have also inadvertently led to the discovery of a highly efficient luminescence process (>10% quantum efficiency) that suggests an alternative means of achieving good optical properties in a silicon-based technology.[15] This process originates from excitons localized by the statistical fluctuations in potential that are inherent to the SiGe alloy. The random nature of the SiGe alloy is known to manifest itself in the band edge PL of both bulk[16,17] and strained layers[8] as a broadening of the PL peaks, and a relaxation of the usual wave vector conservation rules to give strong no-phonon transitions despite the indirect band gap. Another consequence of the statistical fluctuation in germanium concentration is the formation of regions rich in germanium, which can act as potential wells for holes. This can be described within the framework of Anderson localization,[18] where the conduction and/or valence band edges are smeared so that a tail in the density of states extends into the forbidden gap. A characteristic energy known as the mobility edge distinguishes between the localized states and the extended states of the pure crystal. At low temperatures, the excitons can become immobilized many kT below this mobility edge. Localized states have been reported in other semiconductor alloys, including $GaAs_xP_{1-x}$,[19-23] CdS_xSe_{1-x},[24] and $Ga_{1-x}Al_xAs$;[25] however, it was not recognized that such localization can lead

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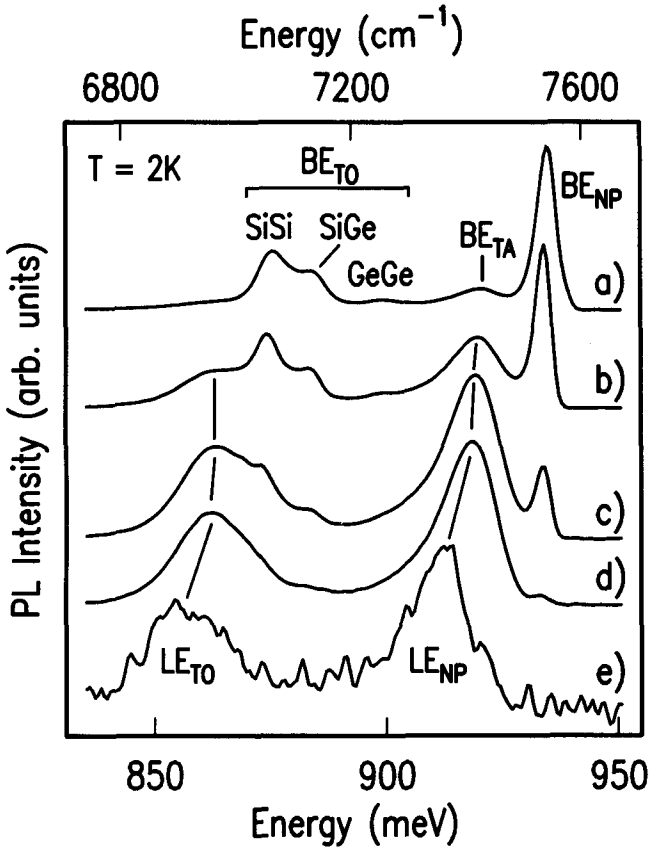

Fig. 1. Emergence of LE_{NP} and phonon replica PL from beneath the BE features under conditions of low excitation power density. Photoluminescence spectra taken at excitation power densities of a) 3.2 W cm^{-2}, b) 0.32 W cm^{-2}, c) 30 mW cm^{-2}, d) 2.3 mW cm^{-2}, and e) 2.4 μW cm^{-2}.

to high radiative efficiency. While Permogorov et al.[26] do mention the possibility of improved efficiency due to localization in CdS_xSe_{1-x}, they neglect to provide any direct measurements to support this supposition.

In this paper we will present further evidence to show that the new PL process in our SiGe/Si samples is consistent with localization by alloy fluctuations and discuss how this leads to the observed high quantum efficiency.

EXPERIMENTAL TECHNIQUES

The SiGe layers were grown epitaxially on <100> silicon by rapid thermal chemical vapor deposition (RTCVD), as described previously.[8,27] Briefly, the SiGe CVD occurs by reacting dichlorosilane in a hydrogen carrier gas with a mixture of germane and hydrogen at 600–625°C, for a nominal growth rate of around 80Å/min. The wafer is suspended inside a quartz tube on quartz pins, without any susceptor or internal heater and is heated with a bank of tungsten halogen lamps located outside the quartz tube. Accurate temperature control during the growth is provided by feedback of in-situ measurements, of the optical absorption of the silicon substrate at 1.3 and 1.55 μm. In all cases, a silicon cap was also deposited to prevent the loss of the SiGe PL signal due to surface recombination.

The PL measurements were taken using a Fourier transform interferometer (Bomem DA8.02) with an InGaAs detector. Above band gap excitation at 488 nm was provided by an argon ion laser. For the time-resolved measurements, the argon laser was pulsed using an acousto-optic modulator. The samples were immersed in super-fluid or boiling liquid helium, except in the temperature studies where they were attached to a temperature controlled silicon block and placed in a flowing helium gas Varitemp dewar. The quantum efficiency was measured using an integrating sphere. The purpose of the sphere is to remove any directional dependence of the emitted PL to give a representative value of emitted flux. This was done by simply placing the sample immersed in liquid helium at the back of a hollow sphere having a diffusely reflecting gold-coated surface. The laser excitation entered through a small hole perpendicular to a port through which only the diffusely reflected PL signal was collected by the interferometer. The intensity of light escaping the sphere and instrumental response were then calibrated by shining incoherent light of a known power density, having approximately the same wavelength as the PL (1.3 μm), into the excitation hole and collecting the signal in the same manner. Both the laser and reference light intensity were determined before being directed into the sphere using a pyroelectric radiometer (Molectron PR-200). The measurements were also corrected for an estimated sample reflectivity at 488 nm of 0.62.

RESULTS

The new PL band and its TO phonon replica were ideally observed under conditions of low excitation density (<100 mW cm^{-2}). Under more intense excitation, the peaks were obscured by the bound exciton PL features typically found in SiGe alloys.[8–14] Figure 1 shows spectra taken at a series of excitation densities from a single 10 nm $Si_{0.75}Ge_{0.25}$ quantum well that has sides linearly graded in germanium fraction over 50 nm, starting with x = 0.13 at the well edge then decreasing to the silicon substrate and cap. The SiGe bound exciton (BE) peaks are labelled in Fig. 1 by BE_{NP}, BE_{TA}, and BE_{TO} for the no-phonon transition, TA phonon replica, and TO phonon replicas, respectively. These transitions correspond to excitons bound to shallow substitutional impurities, such as phosphorus or boron. The no-phonon peak of the new PL process, which we label LE_{NP} for "localized exciton," is shown to emerge from beneath the BE_{TA} phonon replica at low excitation. The peak of the LE_{NP} line in this sample is approximately 20 meV below the BE_{NP}, while in other samples consisting of either single quantum wells or multiple quantum wells, with x between 0.14 and 0.25, this separation ranged anywhere from 12 to 25 meV. The similar intensity of the no-phonon peak relative to the phonon replicas in the LE and BE PL is consistent with the diffuse, shallow nature of potential wells expected for localization due to concentration fluctuations. A similar binding energy resulting from a short range impurity central cell

potential would lead to a much stronger no-phonon intensity.

The LE PL lineshape is asymmetric, having a low energy exponential tail and relatively sharp high energy cutoff that shifted to higher energy with increasing excitation density. This is shown more clearly in Fig. 2 (bottom), where the PL signals have been normalized to give equal intensity in the low energy tail, and a semi-log plot is used to emphasize the exponential lineshape having a 1/e slope of 9.1 meV as indicated. The sharp high energy cutoff has been found to be characteristic of LE PL in other systems.[19,21-24] The exponential tail is also typical of LE, with the literature describing models of localized state systems based on an exponential dependence of the density of states tail on energy.[19,21,24] The shift to higher energy with increasing excitation is consistent with a gradual filling of the density of states, implying that in the case of SiGe alloys, the excitons are able to tunnel or hop between nearby localization centers. The LE lineshape dependence on temperature is also shown on a semi-log scale in Fig. 2 (top). For clarity, these spectra have been modified by subtracting off the overlapping free exciton PL using a high power spectrum, in which the LE PL is negligible. The upper two curves have also been shifted in energy to correct for an estimated band gap shrinkage of 1.5 meV at 40 K and 3 meV at 60 K. As the sample temperature was increased from 4.2 to 60 K, the high energy edge broadened, as expected with an increase in thermal excitations between fluctuations of varying depths at higher temperatures. We did not observe the shift in the LE peak to lower energy with increasing temperature, which has been reported for $GaAs_{1-x}P_x$.[21,22]

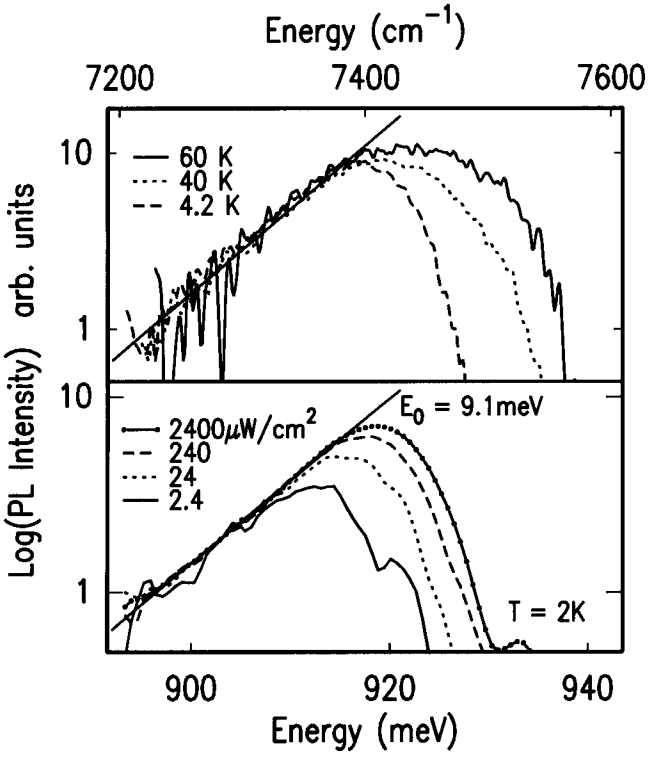

Fig. 2. SiGe LE_{NP} lineshape dependence on temperature (top) and excitation power density (bottom). The PL scales have been normalized to give equal intensity in the low energy tail. In the top set of spectra, the SiGe free exciton PL has been subtracted for clarity. The 40 and 60 K curves have also been shifted by 1.5 and 3 meV, respectively, to account for band gap shrinkage with temperature. The low energy edge is found to decrease exponentially as a function of energy, with a 1/e slope of 9.1 meV as indicated.

While the SiGe and silicon BE PL intensity was found to have the usual slightly sublinear dependence on excitation density, the LE band saturated at very low excitation density (~100 μW cm^{-2}). This saturation behavior has been observed in other alloy LE PL.[21-23,25,26] The saturation may result from an increase in the number of compositional fluctuations binding more than one exciton, so that at high excitation density, Auger recombination again dominates over radiative transitions. Similar behavior has been seen in the binding of more than one exciton by an isoelectronic center in silicon.[28] The LE PL was readily observable even at excitation densities as low as a few μW cm^{-2}, where the usual SiGe and silicon bound or free exciton PL was much too weak to detect. Estimates of the BE PL integrated intensity, obtained by extrapolating down to this low power level, were about 1000 times weaker than the measured LE PL integrated intensity. This prompted us to measure the LE band quantum efficiency directly, with the extraordinary result that the external quantum efficiency of the LE process below saturation (at 12 μW cm^{-2} of excitation) was in fact 11.5 ± 2%, several orders of magnitude larger than typical values for silicon. As discussed below, this high quantum efficiency is consistent with an LE model, while being very difficult to reconcile with typical impurity or defect related processes.

Time-resolved measurements also support the iden-

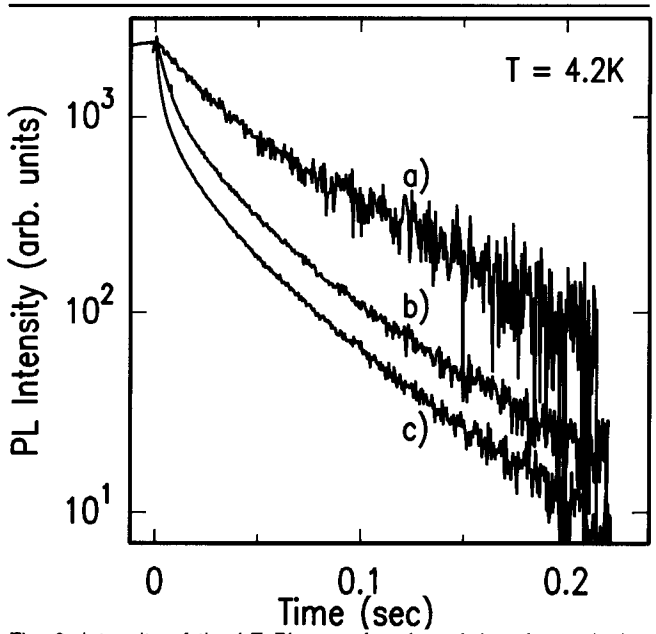

Fig. 3. Intensity of the LE PL as a function of time for excitation densities of a) 1 μW cm^{-2}, b) 3.5 μW cm^{-2} and c) 35 μW cm^{-2}. The decay curves are nonexponential, with a faster decay occuring at high excitation density.

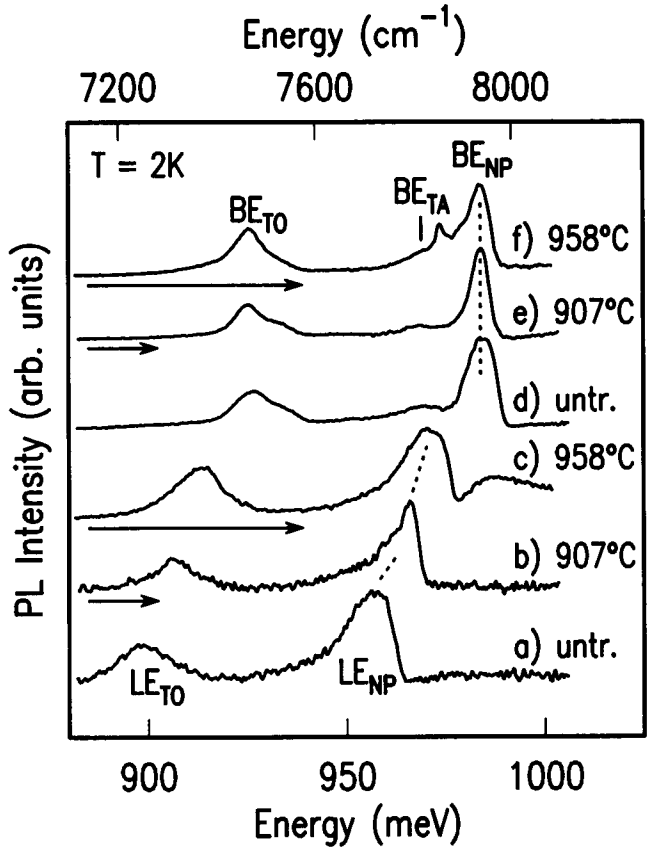

Fig. 4. Photoluminescence spectra of 8.3 nm $Si_{0.8}Ge_{0.2}$ quantum well samples with anneal treatments of a),d) untreated, b),e) 20 min at 907°C and c),f) 20 min at 958°C. The top three curves, taken with high excitation density (6.5 W cm^{-2}) show the usual SiGe BE PL features. The bottom three curves were at low excitation density (25 mW cm^{-2}), at which the LE PL clearly dominates. Spectra b), e) and c), f) were shifted by 17.5 meV and 54 meV, respectively, to line up the SiGe BE_{NP} peaks. The sharp feature above the BE_{TA} in f) and broad band above the LE_{NP} in c) originate from the silicon substrate.

tification of the new process as due to free excitons localized by alloy fluctuations. The decay in PL intensity was measured under conditions of different excitation density, as shown in Fig. 3. These curves represent the total LE PL intensity, with no attempt as yet to study the lifetime behavior at different spectral positions on the peak. The LE PL was found to decay on an extremely long time scale, with an initial 1/e decay of about 3 ms, stretching to tens of ms at later times. This compares well with an estimated radiative lifetime of 1 ms for unlocalized free excitons,[29] and not with the fast decays (~100 ns) typically associated with the Auger transitions of impurity related centers. The long lifetime together with a relative scarcity of localization centers would account for the very low excitation density at which saturation sets in. In agreement with studies in $GaAs_{1-x}P_x$ and $Ga_{1-x}Al_xAs$, the LE are not only long lived but the decay curves are nonexponential[21–23,25] and power dependent.[21,22,25] The nonexponential behavior is thought to arise from a distribution of the probability of scattering by the random potential, which is needed for an allowed no-phonon transition.[21,22,25] The power dependence also follows from an increase in the fast component of the decay curves at higher excitation density given the increase in Auger transitions.

The LE PL features were observed in many samples, including several thicknesses and germanium concentrations in single SiGe layers, as well as multiple quantum well and superlattice structures. In all cases, the epitaxial layers were below the critical thickness for strain relaxation, so misfit dislocations are not thought to play any role. Vescan et al.[13] also report PL features for thin $Si_{0.7}Ge_{0.3}$ quantum wells grown by low pressure CVD that appear to be identical in lineshape and position to the LE PL lines found in our samples (grown by RTCVD). This supports the identification of the PL process as intrinsic to the SiGe alloy rather than resulting from some growth specific defect. While Vescan et al.[13] did not observe the LE PL in quantum well samples having thicknesses greater than 2 nm, this may simply be due to inappropriate excitation conditions. We did not observe the LE PL in any SiGe grown by molecular beam epitaxy (MBE), although as discussed below, the broad band often observed 100 meV below the band gap in MBE material may in fact originate from a related process. There also may be some connection between the LE PL and the L-band identified in bulk relaxed SiGe alloys.[16,17]

The assignment of the LE PL features to an intrinsic process, such as localization by alloy fluctuations, is further supported by persistence of the LE PL band despite annealing at temperatures up to 958°C. The RTCVD epitaxial layers are initially metastable since the rapid thermal processing effectively freezes the atoms into place as the temperature is quickly ramped down. Any clustering of the germanium atoms, vacancies, etc. might then be expected to be eliminated by annealing. Figure 4 compares PL spectra of a), d) an as-grown 8.3 nm $Si_{0.8}Ge_{0.2}$ single quantum well sample with those after a 20 min anneal at b), e) 907°C and c), f) 958°C. Note that the initial SiGe thickness is below the equilibrium critical value (~10 nm, People and Bean[30]), so that the layers should remain fully strained even after annealing. The upper three curves (d, e, f) were taken with a high excitation density (6.5 W cm^{-2}) and thus show the SiGe BE features, while the lower three spectra (a, b, c) correspond to low excitation density (25 mW cm^{-2}) at which the LE PL dominates. The SiGe spectral features of the annealed samples were found to lie to higher energy as indicated by the arrows, having been shifted in the figure so as to align the SiGe BE_{NP} peaks. This observed shift in the SiGe BE PL is consistent with a lowering of the germanium fraction as the germanium atoms diffuse into the silicon substrate and cap. Despite the migration of the silicon and germanium atoms during annealing, the LE peaks do not disappear and shift roughly as expected with the BE luminescence (i.e. with the effective band gap). This confirms that the LE PL features in the as-grown spectrum are due to fluctuations in germanium concentration that are entirely random in nature and, therefore, are maintained even after sample

annealing. The LE PL is somewhat closer to the BE in the annealed samples, perhaps indicating some dependence of the mobility edge on the germanium fraction. However, it is difficult to draw any quantitative conclusions about the LE-BE separation based on this particular set of samples, since the initial SiGe thickness of only 8.3 nm suggests that the situation may be complicated by quantum confinement effects.

DISCUSSION

We have observed a PL process in SiGe that is consistent with localization of excitons by random fluctuations in alloy composition. This conclusion is based on the observation of

- an exponential low energy tail and sharp high energy cut off,
- lineshape dependence on power and temperature,
- long, power dependent, nonexponential decay curves,
- saturation at low excitation power levels, and
- presence in many different sample structures, including annealed.

In addition, the high quantum efficiency of this process directly follows from the exciton confinement. Due to the long free exciton radiative lifetime in silicon (~1 ms[29]), free excitons migrating through the crystal are likely at some time to encounter an impurity, so that nonradiative channels normally dominate over intrinsic recombination even in the highest purity silicon. The likelihood of an LE being in the vicinity of an impurity, and thereby undergoing a nonradiative Auger transition is almost negligible. For example, if we assume a reasonable localization radius of 5 nm and typical doping level of 10^{16} cm^{-3}, the probability of finding an impurity within the LE volume is only 0.5%. Thus, the majority of the LE are expected to decay radiatively, albeit with a very long decay time.

Although the 11.5% quantum efficiency of the LE band is impressive, to be of practical use, several problems must be addressed. Firstly, the saturation power must be increased, by increasing both the number of localization centers and the radiative rate. Also, the LE binding energy due to statistical fluctuations alone is too small, so that thermal quenching occurs at only a few tens of K. Sasaki et al.[31] describe an attempt at artificially creating conditions for Anderson localization in indirect gap AlGaAs using a disordered superlattice structure. For SiGe, this might instead be accomplished by development of a growth process in which the compositional fluctuations are no longer statistical but rather driven by some other means, producing in the limit a "suspension" of pure germanium particles a few nm in radius and separated by an average ≥10 nm. As well as increasing the number of binding centers, this might also increase the radiative rate by confining the holes in much deeper and more abrupt potential wells, thus increasing the likelihood of no-phonon processes. The greater well depth would also stabilize the LE emission up to much higher temperatures.

We can speculate that such a process may already explain the broad, relatively efficient PL band observed 100 meV below the alloy band gap in some MBE samples (see for example Noël et al.[32]). We have directly measured a PL quantum efficiency of 1.9 ± 0.35% for this band, which however represents a lower bound since the sample appeared to have degraded somewhat over time. Despite the lower quantum efficiency, the MBE sample can emit much more PL than the RTCVD material since it does not saturate at low power density. Also, the MBE band appears to be associated with a much deeper and shorter range potential than the RTCVD LE PL. This is based on its larger energy shift from the alloy band gap, its predominantly no-phonon nature and, shorter PL lifetime (~30 μs). These characteristics are consistent with an LE model in which the germanium concentration fluctuations are much larger than those produced by random statistics. In fact, there is already evidence that the emission process involved in the MBE band may be related to compositional fluctuations. Its presence has been correlated with the appearance of platelets, which might in fact be regions rich in germanium, in transmission electron micrographs.[9] There is also a large body of literature describing islanding phenomena in MBE growth in the Si-Ge system.[33–36]

In conclusion, we have demonstrated that high quantum efficiency (>10%) can be achieved in SiGe through the elimination of nonradiative channels, rather than by increasing the radiative rate. A highly efficient PL process was observed in RTCVD SiGe that we identified as due to excitons localized by random fluctuations in germanium concentration. The deep, broad, relatively efficient PL band observed in MBE material may also be due to a related process and as such give clues toward an MBE growth process from which practical applications might evolve. While the MBE growth may inherently already favor the germanium clustering, similar effects might be developed in CVD material with careful consideration of growth parameters.

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