Retraction Notice

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Phosphorus Dopant Distribution in Highly N-Doped Ge Film on Si(001) Substrate Using Specific GaP Solid Source

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Abstract

Germanium (Ge) is a pseudo indirect band gap material due to a tiny difference (~140 meV) between the direct and indirect band gap. However, Ge could have greatly enhanced photoluminescence at room temperature by inducing a tensile strain and a heavy n-doping level. In this study, Ge growth on Si(100) wafer using molecular beam epitaxial (MBE) method and a high n-doping level in Ge was achieved owning to using GaP decomposition source. Phosphorus dopant distribution in Ge film is investigated by Atomic Probe Tomographic (APT) reconstruction. The dependence of optical property on Ge film thickness is also studied. An activated phosphorus concentration can be obtained up to more than 2×10^{19} atoms·cm^{-3} confirmed by Hall effect measurement. This result opens a new perspective of realization of semiconductor optoelectronic devices based on silicon technology.

Keywords

Heavy N-Doping, Germanium, Dopant Distribution, GaP Source, Optoelectronic Application

1. Introduction

In the last few years, research on the tensile strained and n-doped Ge thin film on Si substrate has been the subject of many investigations with the hope to realize an Ge active layer in optoelectronic devices totally compatible with CMOS technology [1] [2] [3] [4] [5]. It has been shown that Ge could become direct band gap material when applying a tensile strained value of 1.9% on Ge layer [6]. However, Ge will emit a photon with wavelength of about 2500 nm, which is out of the wavelength of telecommunication band. Addition, it's a big challenge to get such high tensile strained value while conserving a good quality crystalline of Ge.

Another approach to enhance the efficient radiative recombination of Ge film is fulfilling the energy level of the indirect band gap by doping electron from group

V elements such as P, As or Sb. With a high n-doping level of about 7 × 10^{19} a·cm^{-3} [7], the energy state of the indirect band gap, which is equivalent to the lowest energy level at the bottom of the direct band gap is fulfilled. Thus, injected electrons will have a higher probability to occupy the direct Γ valley and a high efficiency of radiative recombination would be obtained. Nevertheless, remaining a big challenge is to achieve a high n-doping level due to low solubility of group V-element in Ge [8].

In this study, P is used for n-doping process because the solubility of phosphorus molecular in Ge is the highest among V-group elements with intermediate temperature range of about 500˚C - 600˚C [8]. However, normal method for n-doped Ge film from phosphorus is by mean of using PH_3 gas, which produces tetrahedral phosphorus molecule with low sticking coefficient and the highest doping concentration only obtained in the range of 1 × 10^{18} - 1 × 10^{19} at·cm^{-3}. In this work, we implement n-doped process by using GaP specific decomposition solid source, which produces P_2 molecule with sticking coefficient 10 times higher than that of P_4 [9] [10]. It is shown that activated electron concentration up to 2 × 10^{19} at·cm^{-3} can be obtained confirming by both Hall Effect measurement and band gap narrowing phenomenon.

2. Experimental Detail

Ge epilayer growth was implemented in a standard MBE system with a base pressure lower than 2 × 10^{-10} torr. The growth chamber is equipped with a 30 keV reflection high-energy electron diffraction (RHEED) apparatus allowing to observe in-situ and in real-time the Ge growth mode. Ge was evaporate from a two zone heated Knudsen effusion cell with deposited rate in range of about 2 - 5 nm·min^{-1}.

The substrates were flat, n-type Si(001) wafers. Cleaning of the substrate surface follows chemical method at the first step with a cycle of oxidation in a hot HNO_3 acid and oxide removal in a dilute HF solution to etch residual carbon contaminants on the surface. After eliminating a rough oxide layer, a very thin and smooth oxide layer is formed in an HCl:H_2O_2:H_2O solution to protect the Si surface from hydrocarbon adsorption during the sample loading process.

The second step is heating process in ultra high vacuum to evaporate SiO_2 thin layer at a temperature of about 650˚C before flash annealing at 900˚C in 5 seconds. After this step, the Si surface exposes a well-developed (2 × 1) reconstruction. The substrate temperature was estimated using a thermal-couple in contact with the backside of the Si wafer with accuracy of about ±20˚C.

The film resistivity was measured at room temperature using a standard four-point probe technique. Gold (Au) contact with a surface of about 3 mm^2 were prepared on the top of the Ge surface using conventional optical lithography to insure the reproducibility of the resistivity measurement.

The PL is measured with a 532 nm laser focused on the sample surface. The PL signal is measured with an In GaAs detector. PL spectra were recorded at room temperature. Active phosphorus concentration is calculated by mean of using Hall Effect measurement and reconfirming by band gap narrowing phenomenon. Distribution of phosphorus dopants was investigated owning to tomographic APT reconstruction.

3. Results and Discussion

In order to evaluate the efficiency of n-doping process from the decomposition of GaP, one of the first parameters needing to be controlled is the temperature range of the GaP cell in which only phosphorus can evaporate. Indeed, GaP is decomposed into Ga and P_2 molecules and at an intermediate temperature range it is expected that only P_2 can escape from the cell while Ga be trapped by a cap placed on top of the cell [10].

Figure 1 displays the evolution of the room-temperature photoluminescence spectrum versus the temperature of the GaP cell. For all samples, the substrate temperature is chosen to be 300˚C and the film thickness is 100 nm. The temperature of the GaP source increases from 600˚C to 750˚C. After growth, all samples were annealed in the growth chamber at 650˚C during 60 seconds to activate dopants. As can be seen from the figure, the photoluminescence intensity increases with increasing the temperature of the GaP source from 600˚C to 725˚C and the highest PL intensity is obtained at 725˚C. For the GaP source at 750˚C, the PL is found to decrease. Thus, the PL result indicates that above 725˚C the Ga trap from the GaP cell becomes less efficient.

To investigate the effect of the doping level versus the substrate temperature as well the role of sticking coefficient of P_2 on Si substrate, we have therefore kept the GaP source at a constant temperature of 725˚C. Figure 2 displays the evolution of the film resistivity versus the substrate temperature. We note that I-V measurements were carried out at room temperature and all samples have a total thickness of 100 nm (30 nm thick undoped Ge layer deposited at 300˚C to

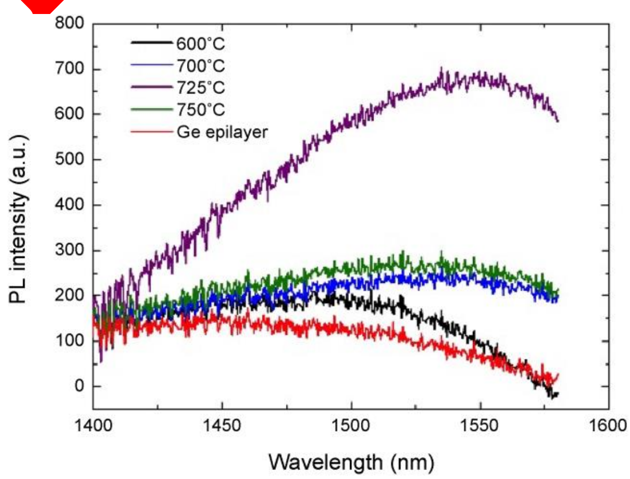

Figure 1. Evolution of the room-temperature photoluminescence spectrum versus the temperature of the GaP cell.

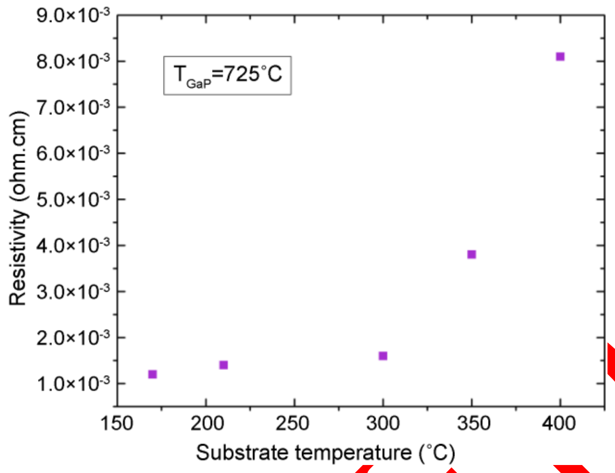

Figure 2. Evolution of the Ge layer resistivity versus the substrate temperature.

form a smooth and strain relaxed buffer layer, followed by a 70 nm P-doped Ge film deposited at various substrate temperatures). It can be clearly seen that the resistivity decreases when increasing the substrate temperature from 170˚C to 450˚C and the lowest resistivity is obtained at a substrate temperature of 170˚C. This result is somewhat in contrast to the reference [11] which indicates that the highest solubility of P in Ge is at 580˚C. It is worth noting that based on these data, we have preformed, at the beginning, numerous doping experiences around 580˚C, the highest solubility temperature of phosphorus. However, the optical and electrical results of the corresponding samples were not as good as expected; we thus decided to investigate the P doping as function of the substrate temperature. We believe the above data of the doping solubility in Ge is only valid for a low concentration range of dopants.

To explain our above results, we suppose that the efficiency of phosphorus doping may depend on two main parameters: the dopant solubility in a matrix and the sticking coefficient of dopants on the film surface. These two parameters are probably competing. The sticking coefficient of an atom or molecule on a substrate surface increases with decreasing the substrate temperature. Since our results reveal that P doping is more favorable at low substrate temperatures, it appears that the sticking coefficient of the P_2 molecules is the dominant parameter determining the phosphorus doping level in Ge film.

We also investigate the effect of film thickness on the optical properties of P doped Ge layers. **Figure 3** shows the evolution of the PL spectrum versus the film thickness. Interestingly, the figure reveals that the PL intensity quickly increases more than 5 times when the film thickness increases from 100 to 530 nm and then slowly increases for further increase of the film thickness from 530 to 1150 nm (about 1.2 times). Taking into account the deposition time of about 3.5 - 4 hours that needs to grow a micrometer thick film by MBE, a film thickness of about 500 nm appears to be a good compromise for Ge applications in optoelectronics. The rapid increase of the PL intensity when increasing the film thickness from 100 to 530 nm can be explained by an increase of the tensile strain and in

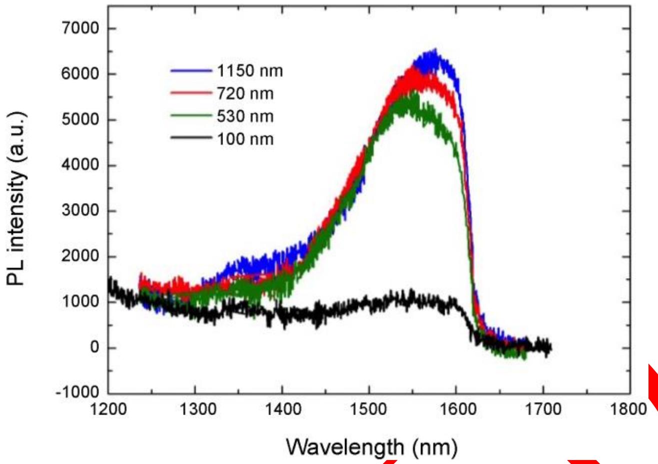

Figure 3. Evolution of the room-temperature photoluminescence spectrum versus the film thickness of P-doped Ge samples.

particular by a better crystalline quality of the layer. Indeed, as the Ge/Si interface region contains a high density of misfit dislocations, when the film becomes thick enough, the optically probed material is far from these defected regions giving a better optical response. We note that for an excitation laser wavelength of 532 nm used in this work, the penetration length of photons in Ge is in the order of about 10 nm. Thus, mainly a very thin region of the film surface is sensitive to the PL measurements. Therefore, when the film thickness reaches a value of about 500 nm, the film surface becomes far enough from the interface region and as a consequent, the PL signal will slightly increase with a small increase of the average tensile strain in the film [12].

The above results have allowed us to set up key parameters of the growth condition to obtain efficient emission of the Ge direct band gap, such as the temperature of the doping GaP source (725˚C), the substrate temperature (around 170˚C) and the film thickness (around 500 nm). More importantly, the above results imply that the key parameter to get a high electron concentration is the sticking coefficient of the P_2 molecule, which is more important than its solubility (which is highest at 580˚C).

According to previous studies, when Ge is under degenerate doping, *i.e.* when the n-type doping concentration is higher than 1×10^{19} cm^{-3}, a clear red shift in emission wavelength is observed. The phenomenon is called "band gap narrowing" [13] [14] [15]. Thus, from the shift of the emitted wavelength, one can evaluate the activated electron concentration. In **Figure 4**, at 170˚C of substrate temperature and 725˚C of GaP cell, the PL spectrum peak is located at around 1580 nm (*i.e.* the corresponding energy is 0.785 eV). This transition can be attributed to arise from the direct band gap radiative recombinations of the n-doped Ge layer. As compared to the energy maximum around 0.810 eV, arising from the direct band gap emission narrowing at high n-doping levels. Taken into account a tensile strain of about 0.10% in our samples (deduced from XRD measurements) and with a maximum of the PL spectrum located at 1580 nm, we can deduce an activated electron concentration of about 2×10^{19} $e \cdot cm^{-3}$. The value of the electron concentration is in good agreement with that obtained from Hall measurements reported in Table 1 and shown in Figure 5. We note that for

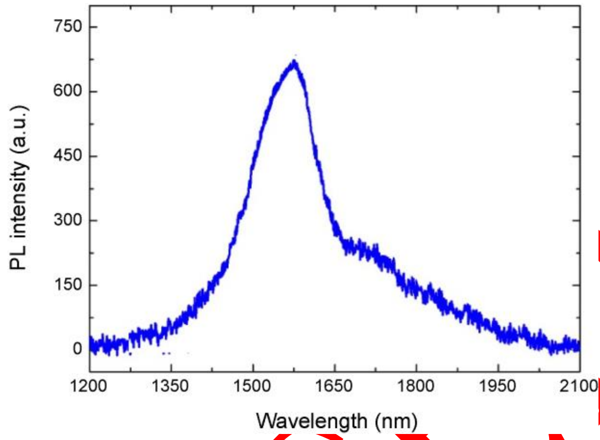

Figure 4. Room-temperature PL spectrum of a Ge layer doped with P. The film thickness is 600 nm, the substrate temperature is 170˚C and the temperatures of GaP cell is 725˚C.

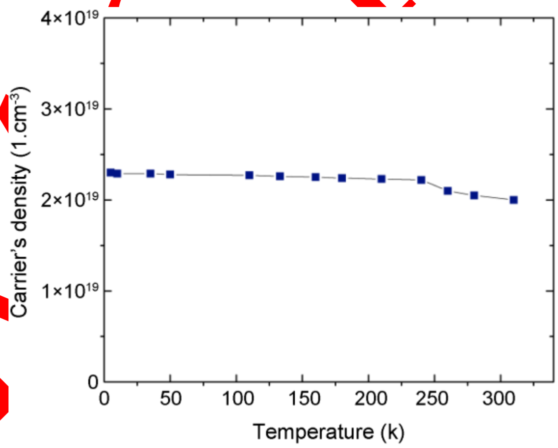

Figure 5. Dependence of carrier's density on measurement temperature.

Table 1. Hall measurements of the carrier concentration, electron mobility and other electrical parameters of a Ge layer, which is doped with P at a substrate temperature of 170˚C.

Sample	**A**	
I source (A)	0.001	0.01
Carrier Concentration (cm^{-3})	**2.07E+19**	**2.06E+19**
Hall Mobility (cm^3/V·s)	**221,769**	**221,925**
Carrier Type	n	n
Resistivity (ohm·cm)	0.000693	0.000693
T (K)	300	300
Hall Coefficient (cm^3/C)	−0.153694	−0.153769
Layer Thickness (nm)	1150	1150

Hall measurements, we have grown thick samples (1150 nm) on a SOI substrate (Silicon On Insulator) of unstrained and un-doped Ge, we observe here a redshift of 25 meV, which can be attributed to band gap (silicon on oxide) substrate to avoid any transport contribution coming from the substrate.

We now discuss about distribution of phosphorus dopants in Ge film by mean of using tomographic APT reconstruction. **Figure 6** represents 2D-tomographic APT reconstruction of P doped Ge on SOI substrate grown at 300˚C. Ge and P atoms are found to distribute quite homogeneously within the microtip along the deposition depth (500 nm). We can also observe that the region of the Ge buffer layer is reinforced by the segregation of P atoms at the interfaces. Thermal annealing is a well-known method for activating dopant atoms within the semiconductors. For an active diffusion occurring, the temperature should be high enough to overcome energy barrier related to atomic motion. We performed rapid thermal annealing at 650˚C for 60 s.

Figure 7(a) shows 2D-tomographic APT reconstruction of the microtip after annealing. From these images, we can see a uniform distribution of P atoms within the sample. Upon annealing, the dislocation lines inside the Ge epilayer no longer appear. The segregation of dopant atoms at the boundaries of Ge buffer layer and Si substrate are also greatly reduced.

From concentration profile of P along the tip (**Figure 8**), we can recognize the

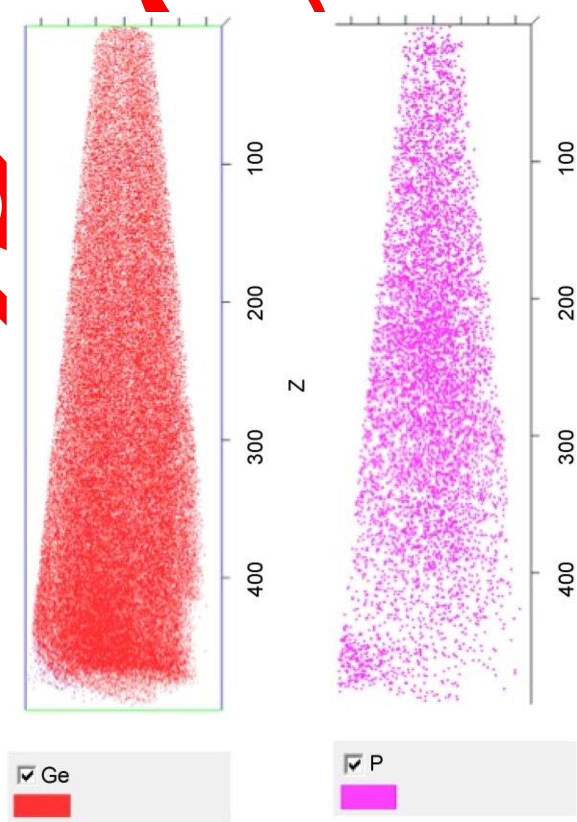

Figure 6. 2D-tomographic APT reconstruction of P doped Ge film on SOI substrate at 300˚C. Each dot represents a single detected atom. Elements are colored coded: germanium red, phosphorous pink.

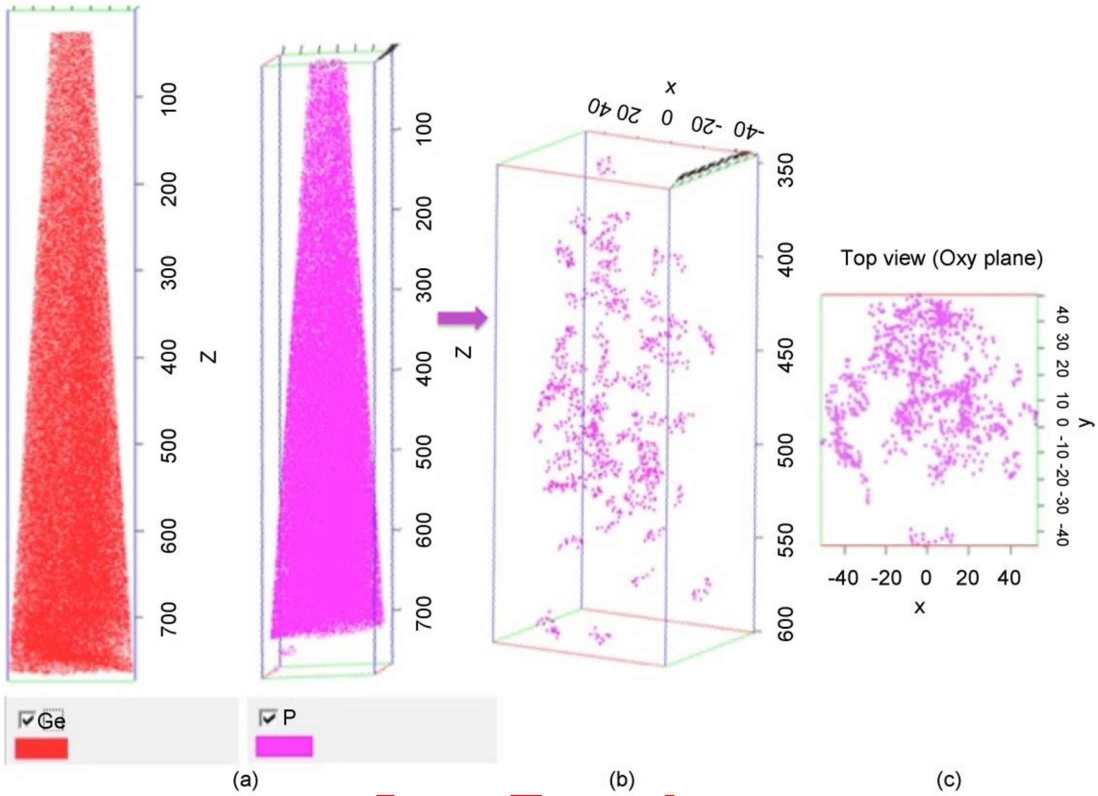

Figure 7. (a) 2D-tomographic APT reconstruction of P doped Ge grown on SOI at 300˚C followed by thermal annealing at 650˚C for 60 s. Each dot represents a single detected atom. Elements are colored as follows: germanium red, phosphorous pink, (b) 3D distribution of P clusters inside the tip from 350 nm to 600 nm, (c) Top view from Oxy plane of the cluster analysis.

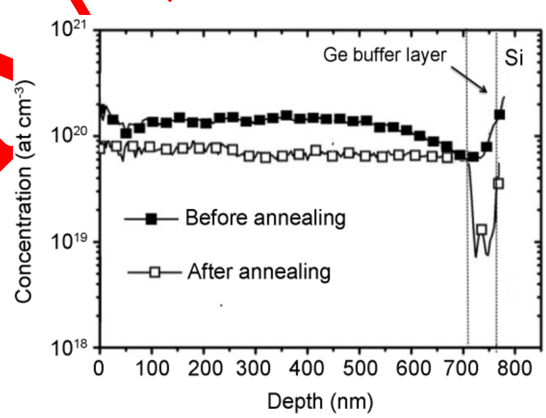

Figure 8. Concentration profiles of P in Ge film before and after thermal annealing along the cylindrical unit in APT reconstruction.

drop by one order of magnitude of P concentration compared to the sample before annealing due to the out-diffusion effect. The average concentration of P is about 7.95 × 10^{19} atoms/cm^3 (before annealing, the P concentration is 1.37 × 10^{20} atoms·cm^{-3}) with a little variation along the deposition depth.

It is worth noting that according to the Hall measurements, which reveal an activated dopant concentration of about 2 × 10^{19} cm^{-3}, it means that about 5.95 × 10^{19} atoms/cm^3 are still in the interstitial sites that have not been activated yet. The cluster analysis was done for P atoms, and surprisingly, we found that P atoms had formed into clusters. From **Figure 7(b)** and **Figure 7(c)**, we also found the formation of clusters. From the cluster statistics, the maximum separation between each cluster atom D_{max}, and the minimum number of atoms per cluster N_{min} are 3.5 nm and 8 atoms/cluster, respectively. As demonstrated in the 3D atom map, the P clusters distribute widely in the whole area of the 750 nm microtip with 254 clusters. The average number of atoms per cluster is about 14 and the density of clusters is approximately 6.2×10^{16} clusters/cm^3. From the top view presented in **Figure 7(c)**, the clusters of P atoms also distribute non-un- iformly within the microtip. Compared to the case of free thermal annealing, the formation of P clusters after annealing shows that P atoms tend to gather together forming small P communities. Indeed, recent experimental studies have shown that the diffusion of n-dopants (P, As and Sb) in Ge have been attributed to vacancy related mechanism. This is a consequence of the lower formation energy of a vacancy (1.88 eV) compared to an interstitial (3.07 eV) in Ge.

4. Conclusion

A new approach to increase P concentration in Ge has been implemented by using specific GaP solid source. The highest activated electron concentration obtained up to 2×10^{19} e/cm^3 by the Hall Effect measurement. This result can be achieved with the following growth condition: the substrate temperature is 170˚C and the GaP source temperature is 725˚C. The distribution of P dopant has been studied by tomographic ATP reconstruction. It is shown that P atoms precipitate into clusters with density of about 6.2×10^{16}/cm^3 and cluster size is approximately 16 atoms per cluster. It means that, after thermal annealing, P atoms tend to gather together forming small P aggregates.

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