Supplementary Information

Promising modulation of self-assembled Ge-rich QDs by ultra-heavy phosphorus doping

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S1. Structure schematic of SiGe alloy film with embedded P-doped Ge-rich QDs.
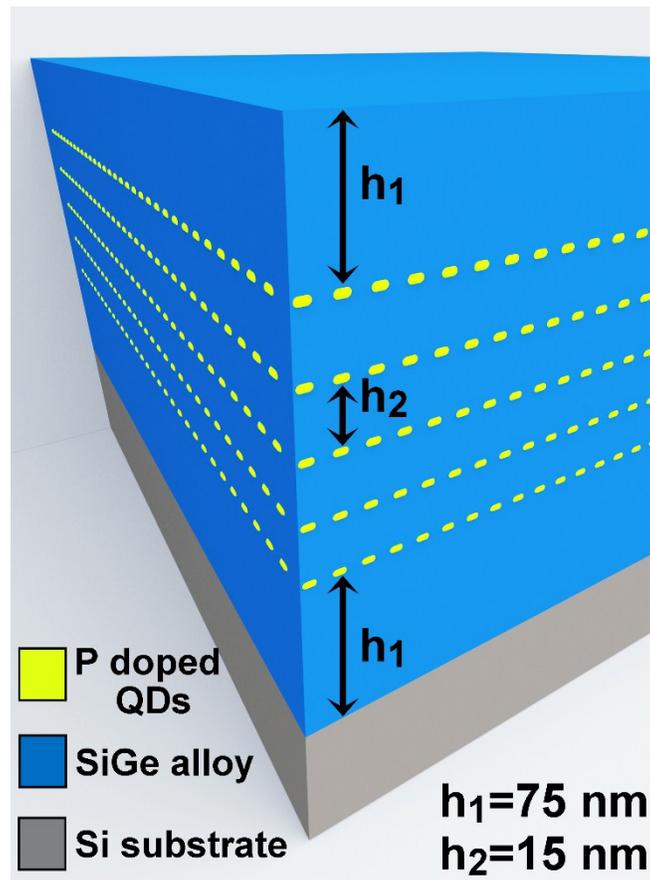
Fig. S1. Structure schematic of SiGe alloy film with embedded P-doped Ge-rich QDs.

S2. Thermodynamic and kinetic effects of dopant on self-assembled QDs

The improved uniformity and the reduced volume of P-doped Ge-rich QDs are obtained in comparison with the undoped ones. These results indicate that the ultra-heavy P doping can considerably affect the growth of Ge-rich QDs. The inherent mechanism can be explained in terms of thermodynamic and kinetic effects. It has been found that some group-V atoms (*e.g.* As) on a surface can affect the growth of Ge-rich QDs due to the reduction of the surface energy.[1, 2] We argue that the P doping can also reduce the surface energy via saturating some dangling bonds on the surface. Accordingly, it can favour the two-dimensional growth, and in turn delay the onset of QDs formation.

Thus, under the same conditions of growth rate, temperature and duration, the average height of P-doped QDs is smaller than that of undoped ones, as demonstrated in Figs. 1b and 1d shown in the main text. The total volume of all P-doped QDs is less than that of all undoped ones.

Taking into account the growth kinetics, the dopant P can reduce the surface diffusion length (L) of Ge adatoms. The L of Ge adatoms on the surface without P atoms is generally given by,[3]

$$L = (D\tau)^{\frac{1}{2}}, D = a^2 v \exp\left(-\frac{E_{Ge}^{Ge}}{k_b T}\right) \qquad (1)$$

Where $D, \tau, a, v, E_{Ge}^{Ge}, k_b, T$ are the diffusion coefficient, diffusion time, the lateral motion (3.84Å) corresponding to each hop of an adatom, the frequency prefactor, the activation energy of Ge adatom for diffusion on a Ge surface, the Boltzmann constant, and the temperature, respectively. In the case of ultra-heavy P doping during Ge growth, the vertical exchange between Ge adatoms and P atoms located in the subsurface should be considered. It results in an external energy barrier E_{ex} for the migration of Ge adatoms on the surface. Accordingly, the effective energy barrier for the diffusion of Ge adatoms on a surface with P atoms is $E_P^{Ge} + E_{ex}$,[4] where E_P^{Ge} is the activation energy of Ge adatom diffusion over a P atom. The mean surface diffusion coefficient (D_P) of Ge adatoms on the surface containing P and Ge atoms can then be given by,[4]

$$D_P = a^2 v \left[x \exp\left(-\frac{E_P^{Ge} + E_{ex}}{k_b T}\right) + (1-x)\exp\left(-\frac{E_{Ge}^{Ge}}{k_b T}\right)\right] \qquad (2)$$

Where, x is the mean coverage of P atoms on the surface (0<x<1). The mean surface diffusion length L_P can then be given by,

$$L_P \approx \left\{a^2 v \tau \left[x \exp\left(-\frac{E_{Ge} + E_{ex}}{k_b T}\right) + (1-x)\exp\left(-\frac{E_{Ge}}{k_b T}\right)\right]\right\}^{\frac{1}{2}} \qquad (3)$$

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where $E_{Ge} = E_{Ge}^{Ge} \approx E_P^{Ge}$, $E_{Ge} \ll E_{ex}$.[1] Comparing Eq. 1 and Eq. 3, it can be seen that L_p is smaller than L as x>0, particularly for the rather large x value due to the ultra-heavy P doping. As a result, the Ge adatoms available for the nucleation and the subsequent growth of QDs from the nearby region is reduced by the ultra-heavy P doping. Under the same conditions of growth rate, temperature and the same amount of deposited Ge, the P-doped QDs can be generally smaller than undoped ones. In addition, a thicker wetting layer can appear due to the P doping. It facilitates the simultaneous nucleation of QDs and the interaction among QDs, which favour the homogeneous growth of P-doped QDs. Thus, the uniformity of P-doped QDs can be better than that of undoped ones.

References

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