Stress relaxation scenario for buried quantum dots

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(Received 20 February 2009; published 10 June 2009)

We report on theoretical and experimental studies of general critical conditions for the onset of relaxation in stressed quantum dots (QDs) embedded into a crystalline matrix. The fingerprint of the relaxation scenario is the formation of specific satellite dislocation loops. The scenario is applicable to both the QDs nucleated and ripened in the bulk and the QDs formed on the surface and then buried by the overgrowth. The results demonstrate that the critical relaxation radius for buried QDs is larger than the critical thickness for stressed lattice-mismatched films or surface islands.

DOI: 10.1103/PhysRevB.79.233304 PACS number(s): 68.65.Hb, 81.07.Ta

Self-assembled nanoislands and nanoinclusions often referred to as quantum dots (QDs) have attracted a lot of attention owing a wide variety of their applications in electronics and a number of new physical phenomena related to their atomic structure, electronic, and optical properties.[1,2] The QDs, being self-assembled either on the surface or in the bulk, are usually elastically strained due to a mismatch in the lattice parameters of the QD (a^{QD}) and the adjacent host material (a^{mat}). Related to elastic strains mechanical stresses and strain energy are responsible for the interaction among QDs and for their vertical and lateral ordering,[3] as well as for effects of a rearrangement in the atomic structure of the QD, adjacent matrix, and/or their interface including the change in the QD shapes and phase intermixing.[4–6]

High strain energy can cause stress relaxation, which usually proceeds via generation and motion of dislocations. In the past, the stress relaxation phenomenon was well documented experimentally and analyzed theoretically for a variety of inclusions with characteristic sizes from 1 to 20 μm, which were embedded into different matrices (see, for instance, Refs. 7–10, and references therein). At this size scale, the mismatch between the inclusion and matrix, for instance, due to the expansion under thermal cycling, can create a high strain energy that results in punching large dislocation pileups. Several mechanisms were proposed for the dislocation loop punching, which were analyzed using energy and force balance criteria.[7–12] While critical conditions for a single event of the dislocation loop formation were found in some cases,[7,11,12] the papers mentioned above are mainly focused on the parameters of the plastic zones, which change the mechanical properties of the composite materials.

The critical conditions for the dislocation formation onset have become of great interest with the progress in the technology of semiconductor QD with characteristic sizes from 1 to 20 nm. For such objects, the first single event of the dislocation formation drastically changes the strain-stress field, electronic structure, and optical properties. The semiconductor QDs are commonly formed on the free surface. This fact gives rise to the extensive experimental and theoretical study of the stress relaxation phenomenon in surface islands.[13–16] The common scenario of stress relaxation for such QDs appeared to be similar to that for thin lattice-mismatched layers and involves dislocations, which either nucleate at nanoisland surface and then glide or climb toward the interface or are injected from the island edge along the interface.

Most of semiconductor devices and research structures utilize QDs buried in the active area. That is possible by the overgrowth of the surface QDs, such as InAs QDs in GaAs formed in Stranski-Krastanow mode,[17] as well QDs can be self-organized in the bulk of a semiconductor film, such as As and AsSb nanoinclusions in GaAs,[18,19] inclusions of P in Ge crystals,[20] and FeO precipitates in MgO.[21] In all cases, the relaxation of initially coherent QDs was found to be possible in the bulk under certain conditions[17–21] via the formation of satellite dislocation loops (SDLs) in a close vicinity of each relaxed QD. The SDLs at nanoscale QDs seem to be apparently different from both the dislocation loops punched by larger inclusions[7–10] and the dislocations formed at strained surface islands.[13–16]

In this Brief Report, we propose a general scenario of a single event of stress relaxation for a buried QD, which is self-assembled in the bulk of a crystalline matrix or is produced by the overgrowth of initially coherent surface island. We demonstrate the qualitative and quantitative difference of stress relaxation for buried QDs compared to the cases of surface islands and lattice-mismatched layers, on one hand, and large inclusions, on the other hand.

Let us consider a general stress relaxation scenario, which involves a SDL and a stressed QD. Taking into account their characteristic sizes, we can use the continuum elasticity approach, which appeared to be reasonably accurate for such objects.[3] The validity of this approach will be verified by the comparison of our calculations with the experimental data. The QD occupying a compact region Ω in a bulk matrix can be characterized by so-called *eigenstrain* tensor[22] $\boldsymbol{\varepsilon}^m(\Omega) = \varepsilon^m_{ij}\delta(\Omega)$ with the components defined by the mismatch between the QD and the matrix crystal lattice parameters. For such an object, the problem of elasticity can be solved by the Mura technique[23] with the QD shape, eigenstrain, and elastic modules as parameters. In case of elastic isotropy, the contribution of QD elastic fields to the Gibbs free energy of the system can be written in a general form as

$$E_{QD} = cG\varepsilon^2 V, \tag{1}$$

where V is the QD volume, ε is the characteristic strain of the lattice mismatch $\varepsilon = (a^{QD} - a^{mat})/a^{QD}$, G is the shear modulus, and c is a dimensionless coefficient accounting for the structure of the eigenstrain tensor and for the shape of the region Ω. For the simplest case of a spherical inclusion of

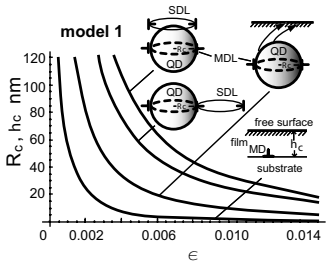

FIG. 1. Critical radii for stress relaxation vs lattice mismatch for different configurations of buried quantum dots QD with equiaxial dilatation with SDL and without SDL, as well as critical thickness for a mismatched film. The schematic models are depicted near corresponding curves. Parameters used for plots: $b=0.3$ nm, $\nu=0.3$, and $\alpha=1$.

radius R_{QD}, i.e., $V=\frac{4\pi}{3}R_{QD}^3$, with either equiaxial $\varepsilon_{ii}^m=\varepsilon(i=x,y,z)$ and $\varepsilon_{ij}^m=0(i\neq j)$ or uniaxial dilatation $\varepsilon_{zz}^m=\varepsilon$ and $\varepsilon_{ij}^m=0(i,j\neq z)$ the coefficient c is $c^e=2(1+\nu)/(1-\nu)$ (Ref. 23) or $c^u=8/15(1-\nu)$,[24] respectively, with ν being the Poisson ratio.

The energy condition of the stress relaxation onset requires the energy of the system $E_{initial}$ with a QD in the initial coherent state to be larger than the energy of the system E_{final} after relaxation, i.e., $E_{initial}\geq E_{final}$. The energy of the initial state can be calculated by Eq. (1) with the appropriate material parameters and coefficient c.

In the final state, we have the QD, SDL, and should consider a rearrangement at the QD/matrix interface. One case of such rearrangement is the formation of misfit dislocation loop (MDL) at the QD/matrix interface. The geometry of this case (model 1) is shown in insets of Fig. 1. The other case (model 2) is schematically shown in the inset of Fig. 2. It can be understood as the formation of a continuous ensemble of MDLs with prescribed surface density, which actually corresponds to a reduction in the mismatch parameter from its initial value ε_{in} to the final value ε_{fin}: $|\varepsilon_{in}|>|\varepsilon_{fin}|$. For a general scenario of stress relaxation for a buried QD, the energy condition evolves into the following:

$$E_{QD}\geq E_{QD}^*+E_{SDL}+E_{MDL}+E_{int}, \tag{2}$$

where E_{QD} and E_{QD}^* are the QD elastic energies before and after relaxation, E_{SDL} and E_{MDL} are the energies of the sat-

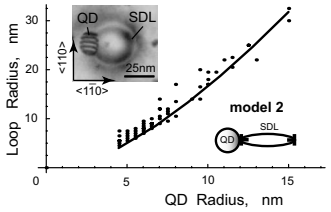

FIG. 2. Theoretical (solid line) and experimental (dots) correlation between the SDL and QD radii for the case of uniaxially strained AsSb QDs in GaAs matrix. The insets show a transmission electron micrograph (TEM) image and schematic model of the AsSb QD associated with prismatic SDL. The SDL lies in (001) plane and has Burgers vector of $\frac{1}{2}[001]a$. The best fit of calculations gives $\varepsilon_{in}=0.035$, which is consistent with the Moiré fringes on the QD TEM contrast. Parameters used for calculations: $b=0.28$ nm, $\nu=0.3$, and $\alpha=1$.

ellite dislocation loop and possible misfit dislocation loop, and E_{int} is the energy of interaction between all objects in the local system of the QD and dislocation loops.

In our calculations, we use the well-established expression for the self-energy of a dislocation loop of the radius R_{DL} and Burgers vector b (Ref. 25)

$$E_{DL}\approx[Gb^2R_{DL}/2(1-\nu)]\ln(8\alpha R_{DL}/b), \tag{3}$$

where $\alpha=1\div4$ accounts for the energy of the dislocation core.[26] The interaction energy between a QD and dislocation loop can be found as an integral over the QD volume V_{QD},

$$E_{int}=-\int_{V_{QD}}\varepsilon_{ij}^m\sigma_{ij}^{DL}dV, \tag{4}$$

where ε_{ij}^m is the eigenstrain defined above and σ_{ij}^{DL} is the stress tensor components for the dislocation loop.[22] The expression for the interaction energy between two dislocation loops is similar to Eq. (4), in which ε_{ij}^m should be replaced by the Burgers vector of the second loop and integration should be performed over the loop area.

In addition to the energy balance (2), we should also consider the material conservation law. For the general case of a relaxed system consisting of the QD and two dislocation loops, the materials conservation requires

$$(\varepsilon_{fin}-\varepsilon_{in})V_{QD}+b_{MDL}^{\perp}S_{MDL}+b_{SDL}^{\perp}S_{SDL}=0, \tag{5}$$

where V_{QD} is the QD volume, $S_{MDL,SDL}$ are the areas of the dislocation loops, and $b_{MDL,SDL}^{\perp}$ are the edge components of the Burgers vectors, which are taken positive for the loops of interstitial type and negative otherwise.

The stress relaxation in the frame of the proposed scenario can be described by solving the system of Eqs. (2) and (5) with corresponding geometric, crystallographic, and physical parameters of the specific QD system. It is worth to investigate the two basic cases introduced above as models 1 and 2, which are relevant to different experimental systems.

Model 1 supposes that $\varepsilon_{in}=\varepsilon_{fin}$; $E_{QD}=E_{QD}^*$ and the materials conservation is met by the simultaneous formation of SDL and MDL. This situation seems to be suitable for such QD/matrix systems as Ge/Si, InAs/GaAs, and others with similar chemical origin of the components and strong chemical bonds at the interface. While many different shapes and orientation relationships are possible for the QD-MDL-SDL system, for the purpose of the model examination we consider two configurations shown in Fig. 1. One configuration, "on top," corresponds to the circular SDL with its center touching the QD of spherical shape. In the other configuration, the SDL and MDL are both located in the equatorial plane. A principal difference of two configurations lies in the mutual position of MDL and SDL. For the on-top position, prismatic SDL can glide away from the QD, living MDL in the equatorial plane. Such configuration was experimentally observed for dislocation loops punched by large inclusions.[7–10] In the "on-side" configuration, the SDL must climb in order to reach a local thermodynamic equilibrium in the QD-MDL-SDL system. Such configuration was experimentally observed for dislocation loops formed in semiconductors with buried nanoscale QDs.[17–21]

Solving Eqs. (2) and (5) for model 1 predicts a threshold for the stress relaxation onset. For simplicity, let us consider the mismatch $\varepsilon_{ii}^m=\varepsilon(i=x,y,z)$, $\varepsilon_{ij}^m=0(i\neq j)$, $c=c^e$, and assume that the SDL and MDL have equal but opposite Burgers vectors that are normal to the plane of the loops. Then, the solution of Eqs. (2) and (5) gives a critical radius R_c in an approximate analytical form,

$$R_c \approx [\beta b/\pi(1+\nu)\varepsilon]\ln(\gamma\alpha R_c/b), \quad (6)$$

where β and γ are dimensionless coefficients; $\beta=1.160$, $\gamma=0.416$ for the on-top and $\beta=0.690$, $\gamma=1.557$ for the on-side configuration.

The physical meaning of R_c and analytical form of Eq. (6) are similar to those of the critical Matthews-Blakeslee thickness h_c for stressed thin films,[27] in which case $\beta=0.125$ and $\gamma=1$. The dependences of the R_c and h_c on the mismatch parameter ε are plotted in Fig. 1. The on-side configuration appears to be preferable for relaxation, when compared to the on-top configuration, since it provides a smaller critical radius for any mismatch ε. For both configurations, the value of R_c is considerably higher than h_c, i.e., buried QDs are much more stable against relaxation than stressed thin films. Plotted in Fig. 1 is also the R_c vs ε in case the material conservation requirement be violated.[28] Such violation reduces R_c; however, it remains considerably larger than h_c.

The other basic case (model 2, Fig. 2) in the proposed scenario implies the formation of SDL accompanied by the reduction in the mismatch $|\varepsilon_{\text{in}}|>|\varepsilon_{\text{fin}}|$ without the formation of a local MDL.[29] This model is relevant to the systems of the QD and matrix with essentially different chemical and crystallographic origin and relatively soft interfaces. Examples of such systems are AsSb QDs in GaAs,[19] inclusions of P in Ge crystals,[20] etc. Insets of Fig. 2 show a schematic model with SDL lying in the equatorial plane of a QD and a transmission electron micrograph of the SDL formed near the AsSb QD in the GaAs matrix.

In model 2, Eqs. (2) and (5) do not have MDL-related terms and the set of these equations determines the total mechanical energy that includes the self-energies of the QD before and after relaxation, self-energy of the SDL, and their interaction energy. Solving Eqs. (2) and (5) predict the existence of a minimum in the total mechanical energy of the conservative QD/matrix system, which occurs at a certain radius of the SDL. This energy minimum results in a nonlinear relation between the radii of the QD and SDL for any given initial mismatch. In the case of the AsSb nanoinclusions in GaAs, the crystallographic geometric and physical parameters of the QD/matrix system have been carefully documented[19] so that the calculation of the mechanical fields and energies can be done in the frame of the considered scenario with uniaxial dilatation ($c=c^u$) and the magnitude of ε_{in} as the only fitting parameter.[29] Figure 2 shows a theoretical curve describing the correlation between R_{SDL} and R_{QD}, which was obtained by numerically solving Eqs. (2) and (5). Comparison with the experimental observations shows a good qualitative and quantitative agreement, when the best fit value $\varepsilon_{\text{in}}=0.035$ is within the bars of the experimental estimate.[19]

Although we are focused on the QDs embedded into the bulk of a crystalline matrix, the presence of free surface cannot be totally ignored. One effect of a free surface on the stress relaxation in a buried QD originates from the violation of the materials conservation law (5). In fact, a surface may act as a source or sink of point defects and atoms. As a result, the mass transport between the surface and QD should modify the energy and material balance between the QD and SDL. The depth, where it should be important, can be estimated as the length of out or in diffusion. The impact of this phenomenon on the critical radius R_c of the QD can be taken into account in the framework of our model by neglecting the formation of SDL.[28] The result of calculations for this case is plotted in Fig. 1. It shows a decrease in R_c when compared to the value for truly bulk QD. Note that the reduced R_c still remains considerably larger than the h_c for stressed thin films.

The other reason for an influence of the nearby surface on the stress relaxation in the bulk is a change in the mechanical fields and energies due to the static equilibrium requirements to the components of the stress tensor on the traction-free surface. As a result, the self-energy of a stressed QD increases, when the QD is buried deeper into the bulk in the matrix. For instance, the energy of a spherical inclusion with $\varepsilon_{ii}^m=\varepsilon(i=x,y,z)$; $\varepsilon_{ij}^m=0(i\neq j)$ in a half space at the distance h from the flat surface is[30]

$$E_{\text{QD}}^s=\frac{8\pi G\varepsilon^2(1+\nu)R_{\text{QD}}^3}{3(1-\nu)}-\frac{4\pi G\varepsilon^2(1+\nu)^2R_{\text{QD}}^3}{9(1-\nu)}\frac{R_{\text{QD}}^3}{h^3}, \quad (7)$$

$$R_{\text{QD}}\leq h,$$

where the first term is the energy of the inclusion in the infinite medium and the second term represents the interaction energy between the inclusion and free surface. Based on Eq. (7), one can expect that relaxation in a stressed QD may be initiated by an overgrowth procedure. Examination of this point requires consideration of the impact of the surface on the self-energies of MDL and SDL and interaction in the QD-SDL-MDL system. The interaction energies $E_{\text{MDL-QD}}^s$, $E_{\text{SLD-QD}}^s$, and $E_{\text{MDL-SDL}}^s$ can be found using Eq. (4) and the elastic energy of a prismatic loop parallel to the free surface can be taken from Ref. 30. Accounting for the results of these calculations, the energy balance (2) should be reconsidered with or without (depending on the ratio between the depth h and the diffusion length) the materials conservation law (5).

The analysis gives a threshold radius R_c for a QD near the free surface, which corresponds to the onset of the stress relaxation process. The R_c cannot be represented in the analytical form similar to Eq. (6). Plotted in Fig. 3 are dependencies of the critical radius R_c on the distance h from the free surface for the two configurations (i.e., on top and on side) of the SDL, as well as for the case when SDL is absent. It appears that the R_c increases or decreases, depending on the configuration, when the QD is buried deeper into the bulk. For the on-side configuration, the R_c decreases with h. It means that in accord of the proposed scenario, a coherent subcritically stressed QD can relax with the formation of SDL and MDL when buried by an apparently harmless overgrowth with the matrix material. The lowest R_c corresponds to the case of the absent SDL, i.e., when the QD exchanges

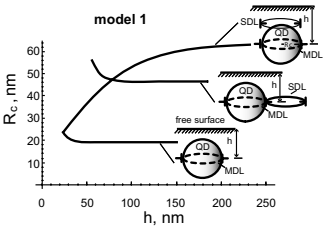

FIG. 3. Critical radius R_c as a function of QD distance h from the free surface. The schematic models are depicted near corresponding curves. Parameters used for plots: $\varepsilon=0.006$, $b=0.3$ nm, $\nu=0.3$, and $\alpha=1$.

the material with open surface and no local equilibrium is achieved. This exchange can be realized by atomic in and out diffusions as well as by gliding of dislocation loops from the QD to the surface. The path of such gliding seems to have no metastable intermediate states. For the QD-SDL-MDL system near the surface in the on-top configuration, it is indicated by the constant increase in the R_c with h (Fig. 3). The R_c in the case of the absent SDL reduces with increasing distance from the surface h. It means that the stress relaxation in an initially coherent surface QD is thermodynamically favorable during the overgrowth whether or not a local equilibrium is achieved.

Stress relaxation was experimentally observed for initially coherent InAs QDs grown in Stranski-Krastanow mode on the surface and then buried in GaAs by a subsequent overgrowth.[17] Transmission electron microscopy revealed the formation of satellite dislocation loops near the QDs in the on-side configuration, which are in qualitative agreement with the proposed scenario. Generally, experimental observations[7–9,17–21] and our calculations show that nanoscale QDs can achieve the lowest free energy with the SDL formation mediated by the local mass transport at short range; whereas relaxation at large inclusions is preferable by the dislocation glide rather than climb due to kinetic limitations for the atomic transport at μm distance.

Potentially, the relaxation process in a stressed buried QD, which is initially coherent, can be triggered by a number of physical phenomena causing an increase in the strain energy. In the case of AsSb QD in GaAs, it is the change in the QD size and lattice mismatch with time due to the Ostwald ripening.[19] Very interesting effects may occur in some systems where phase transformations are possible under appropriate variations made with ambient temperature, pressure, electric, or magnetic fields. It is especially important that the proposed scenario is relevant to the QDs, which are buried in the active area of a QD-based device structure, where the stress relaxation phenomenon is crucial for the device performance.

Atomistic simulations can be applied as complementary tools in the study of the plastic relaxation at stressed inclusions of second phase. As an example of recent attempts, we can mention the work,[31] where the initial yield process in the vicinity of mismatching inclusion in Al was modeled on the atomistic level in the framework of molecular statics simulations. Therefore, one might have a hope that the developing computer facilities will be used in the future for the analysis of the case we have considered in the relaxation phenomena for buried quantum dots.

In conclusion, we have proposed and analyzed a general stress relaxation scenario for stressed nanoscale QDs of different nature embedded into a crystalline matrix. The fingerprint of this scenario is the formation of specific SDLs in a vicinity of the QDs. Configuration of the SDL appeared to be specific when compared to both dislocation loops punched by large inclusions and dislocations formed at relaxed surface islands. We have theoretically analyzed the optimum diameter and threshold of the formation of the SDL for different QD/matrix systems and have verified the model by comparison with experimental observations.

We gratefully acknowledge the support by the Russian Foundation for Basis Research and by the Russian Academy of Sciences.

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