Deformation profile in GaN quantum dots: Medium-energy ion scattering experiments and theoretical calculations

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(Received 25 May 2005; revised manuscript received 5 July 2005; published 1 September 2005)

Medium energy ion scattering (MEIS) has been used to measure at the scale of the monolayer the deformation profile of self-organized GaN quantum dots grown on AlN by molecular-beam epitaxy. The effect of capping the GaN dots by a thin layer of AlN has also been studied. It is shown that GaN dots are partially relaxed in every situation. Capping them with AlN has little effect on the basal plane, as expected, but strongly modifies the strain of the upper part of dots. The experimental results are compared with theoretical calculations, allowing one to conclude that GaN quantum dots experience a nonbiaxial strain, which drastically decreases when going from the basal plane up to the apex of the dots.

DOI: 10.1103/PhysRevB.72.115301 PACS number(s): 81.07.−b, 74.78.Fk

Quantum dots (QDs) of semiconductors are a subject of intense interest for many years due to their specific three-dimensional confinement properties, which make them potentially very attractive for applications such as low threshold lasers,[1] single-photon emission,[2] quantum cryptography, single-electron transistor,[3] or quantum computing. However, this ideal view requires, to become reality, a good control of the size distribution of quantum dots, of their nucleation sites and, in general, of their structural, electrical, and optical properties. In particular, the strain state of QDs embedded in a matrix is an important parameter which governs, to some extent, their optical properties. This is particularly true in the case of the III-nitride semiconductor family. The most usual wurtzite crystallographic phase of these materials exhibits both piezoelectric and spontaneous polarization. Because of the elevated value of the piezoelectric constants,[4] a huge internal electric field is currently observed in nitride heterostructures. This built-in electric field can be as high as several MV/cm in the case of GaN/AlN quantum wells[5] or GaN QDs embedded in AlN.[6,7] Actually, as a consequence of the resulting quantum confined Stark effect, a strong redshift is induced, leading to luminescent emission at energies smaller than the GaN gap value for GaN/AlN quantum wells thicker than about 4 nm as well as for GaN/AlN QDs higher than 2.5 nm.

With the ultimate goal of in-depth understanding and controlling the optical properties of capped and uncapped GaN QDs, this paper addresses the issue of measuring their deformation profile as a function of depth. The technique used, medium energy ion scattering (MEIS), allows one to directly measure the deformation of nanostructures as given by the value c/a at the scale of the monolayer. It has been recently applied to the case of Si-Ge QDs in order to determine their strain state[8] as well as to the case of Ge nanowires deposited on Si.[9] In the present paper, we study the deformation profile of a layer of GaN QDs and will examine the effect of their capping by a thin AlN layer, in connection with the issue of vertical correlation of QDs, which critically depends on the thickness of the spacer between successive layers.[10] The satisfactory agreement between the deformation profile measured experimentally and theoretical calculations performed in the framework of the elastic continuum theory has allowed us to conclude that GaN quantum dots embedded in AlN experience a combination of hydrostatic and biaxial strain leading to a gradient of elastic relaxation along the growth axis.

The samples were grown by plasma-assisted molecular-beam epitaxy in a MECA 2000 chamber equipped with standard effusion cells for Ga and Al. The N flux was produced by dissociation of N_2 in a commercial radio-frequency plasma cell. The substrate was a 2-μm-thick AlN layer deposited on sapphire. After a standard degreasing procedure and acid etching, the substrate was fixed with In on a molybdenum sample holder and introduced in the growth chamber. Prior to the growth of GaN QDs, an AlN buffer layer, about 100 nm thick, was grown in order to improve the surface quality. Then, one plane of GaN QDs was grown by depositing the equivalent of 6 ML of GaN. The growth of the GaN QDs was performed according to the modified Stranski-Krastanov (SK) growth mode.[11] In this procedure, the growth of GaN on AlN in Ga-rich conditions results in the formation of a Ga bilayer on the surface.[12] This metal layer stabilizes the two-dimensional (2D) GaN layer and inhibits the 2D/3D transition, characteristic of the usual SK growth mode, which is observed when growing GaN in N-rich conditions.[13] After depositing 6 ML of GaN, both Ga and N fluxes were suppressed. Then, the desorption of the stabilizing Ga bilayer was followed by a reorganization of the 2D

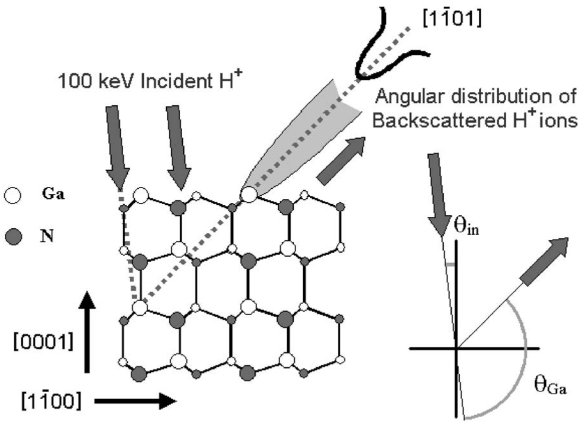

FIG. 1. Scheme of the scattering geometry in the $(11\bar{2}0)$ plane for medium ion energy scattering experiments.

GaN layer and the formation of 3D islands.[11] Three samples were used in the present study: They consist of one plane of uncapped GaN QDs, one plane capped with 10 MLs of AlN, and one plane capped with 20 MLs of AlN. The growth direction was parallel to the [0001] axis of the wurtzite structure. The uncapped QDs were analyzed by atomic-force microscopy (AFM). Their height was estimated to be about 3.0 ± 0.5 nm and their diameter 15 ± 1 nm, leading to an aspect ratio of about 0.2. The density of dots was high, about 1.25×10^{11} cm^2 so that they were almost adjacent.

MEIS measurements were performed using a 101 keV incident H^+ ion beam, $\theta_{in}\sim7°$ off the [0001] direction (see Fig. 1). The energy and angular distribution of scattered protons were measured with a two-dimensional detector,[14] whose energy resolution, $\Delta E/E$, is about 3×10^{-3} and angular resolution is 0.1°. The scattering geometry was chosen in order to observe a range ±10° around the $[1\bar{1}01]$ direction in the $(11\bar{2}0)$ plane.

Figure 2 presents the MEIS angular spectra of the uncapped QD layer taken around the $[1\bar{1}01]$ Ga blocking dip. The Al blocking dip, at a scattering angle $\theta_{Al}=125.3°$ in the AlN substrate far from the GaN/AlN interface was used as a reference for the $[1\bar{1}01]$ direction in relaxed, undistorted material. Each successive spectrum (from top to bottom) in Fig. 2 represents an increase in the energy loss of the backscattered ions and, therefore, gives information about the deformation of Ga sublattice at increasing depth. The highest energy of 96 530 eV corresponds to the ions scattered from the GaN surface, i.e., mostly to the upper part of GaN dots, since the dot density is so high that the contribution of the wetting layer to the MEIS signal in the region corresponding to GaN surface is minor. However, it should be noted that the shape of the $[1\bar{1}01]$ Ga blocking dip at 96 530 eV is different from those at lower energy, exhibiting a satellite dip at about 126.8°, also distinguishable, as a faint shoulder in the spectrum at 96 336 eV. This satellite dip is assigned to the wetting layer, as it will be discussed below. In Fig. 2, the energy of 94 339 eV corresponds to the interface between GaN and AlN. The shifts of the Ga blocking dip θ_{Ga}, with respect to the unstressed value clearly observed in Fig. 2, are indicative

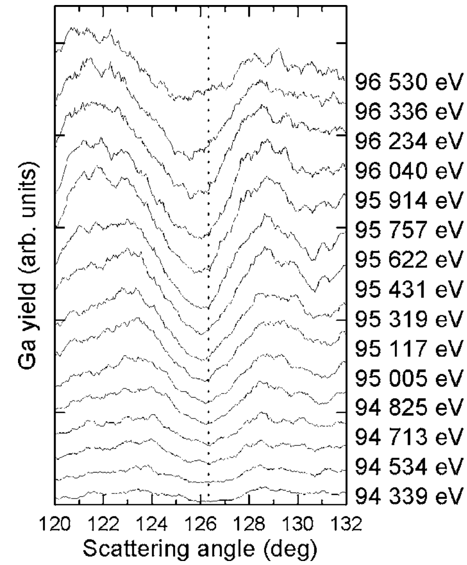

FIG. 2. MEIS angular spectra of the uncapped GaN QDs layer taken for different energies ranging from 96 530 eV (surface of the GaN QD) to 94 339 eV (AlN/GaN interface). The dotted line shows the blocking dip corresponding to the AlN/GaN interface. Note a satellite dip at 126.8° for the 96 530 eV line, which is assigned to the presence of the wetting layer.

of the distorted environment of the Ga atoms in the GaN QDs. The associated strain can be quantified by the magnitude of c/a that can be obtained from θ_{Ga} in the $[1\bar{1}01]$ direction by using the following relation:

$$\mathrm{tg}\left(\theta_{Ga}+\theta_{in}-\frac{\pi}{2}\right)=\frac{c}{a\sqrt{3}}. \quad (1)$$

Therefore, the measurement of the Ga blocking dip as a function of the energy of backscattered particles allows one to determine the deformation of the GaN dots as a function of depth all along the growth direction, with a resolution of about 1 ML.

The results for the ratio c/a as obtained by the above procedure are summarized in Fig. 3(a)–3(c), for the uncapped GaN QDs layer, the single plane capped with 10 ML, of AlN, and the plane capped with 20 ML of AlN, respectively. The depth scale inserted in the three figures is indicative of the resolution of the MEIS experiment and has been obtained from the formula $\Delta E=(dE/dz)\Delta z$, which relates the energy loss ΔE and the depth Δz through the stopping power of H^+ in GaN. However, the measured kinetic energy of an ion scattered from a given depth is distributed over a certain energy range, as a result of the straggling effect in addition to the finite-energy resolution of the detector. As a consequence, the actual energy spectrum corresponding to Ga is wider than predicted by the above formula, and thus the displayed depth scale overestimates the QD's height distribution. The measured profiles of all three samples exhibit a compressive deformation at the QD/substrate (GaN/AlN) interface corresponding to a value of $c/a\approx1.67$. This deformation decreases monotonically with increasing energy (i.e., with decreasing depth) and even drops to $c/a\approx1.61$ at the

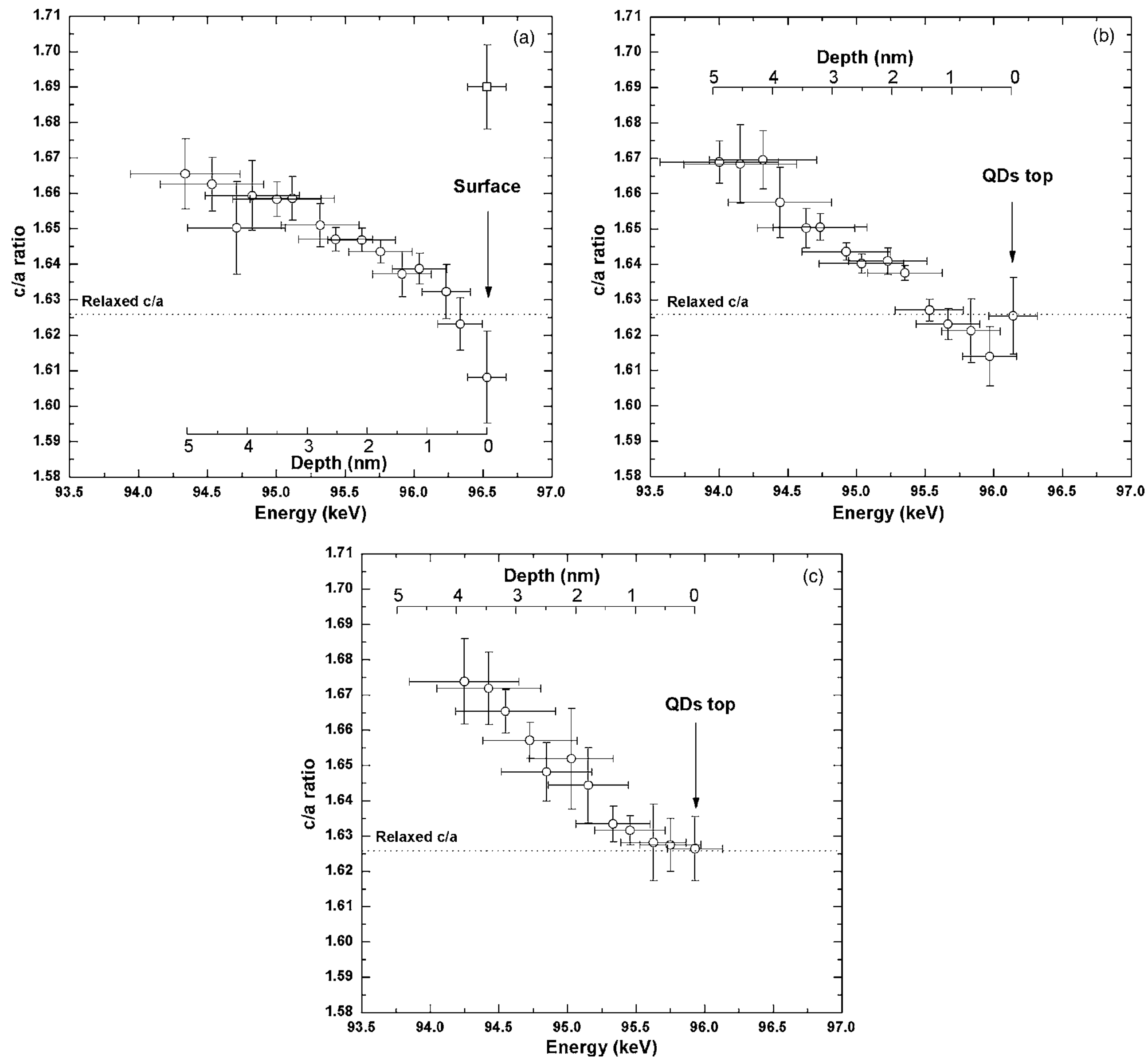

FIG. 3. Depth profile of the ratio c/a in (a) one plane of uncapped GaN QDs, (b) one plane of GaN QDs capped with 10 MLs of AlN, and (c) one plane of GaN QDs capped with 20 ML of AlN. The dotted line indicates the value of c/a corresponding to relaxed, unstrained GaN. The open square in (a) corresponds to the satellite dip at 126.8° in Fig. 2 (96 530 eV), which is assigned to the wetting layer. The horizontal (depth) error bars have been calculated by taking into account both the energy resolution of the detector and the straggling effect affecting the impinging H^+ beam.

surface of the uncapped QDs plane, a value surprisingly below that corresponding to fully relaxed GaN, $c_0/a_0=1.626$. For both samples of QD planes capped with 10 and 20 ML of AlN, the deformation at the top of the dot corresponds approximately to a relaxed material. However, it is important to note that, as will be shown below, these results do not necessarily imply a full relaxation of the GaN QDs.

In addition, in Fig. 3(a), we have plotted the c/a value corresponding to the $[1\bar{1}01]$ Ga satellite blocking dip at about 126.8° in the spectrum recorded at 96 530 eV (see Fig. 2). The agreement with the calculated value for a bidimensional layer experiencing a biaxial strain is remarkable, as a clue that this satellite blocking dip likely corresponds to the wetting layer between and/or far from the dots.

In order to understand the trends observed in the MEIS experiments it appears helpful to dispose of a theoretical model of the strain distribution in the GaN quantum dots. Two general approaches can be used for this purpose, namely, continuum elasticity and atomistic simulations.[15] Whereas the atomistic approach should be preferred in principle, given the nanometric dimensions of the dots, Pryor *et al.* have demonstrated a good correspondence between the results of both methods, with the discrepancies mainly confined to the boundaries of the dot.[16] Therefore, we have chosen to model the strain distribution in a single lattice-mismatched wurtzite GaN/AlN quantum dot. The calculations have been performed in the framework of the elastic continuum theory by using the Eshelby's inclusion method,[17]

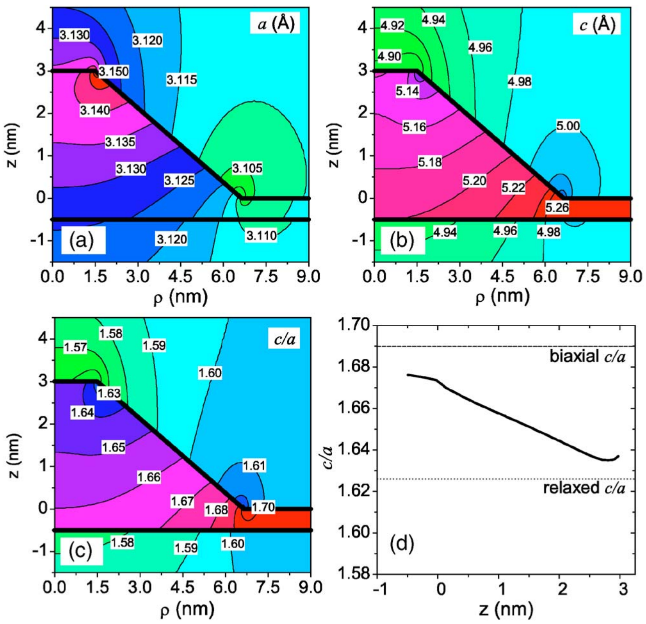

FIG. 4. Two-dimensional contour plots of the lattice parameters a [(a)] and c [(b)]. The numbers in boxes indicate the values of the parameters (in Å) along the different contour lines. The corresponding contour plot of the ratio c/a is shown in (c), and the solid line in (d) displays the calculated depth profile of the in-plane averaged c/a. The dotted line indicates the value of c/a corresponding to relaxed, unstrained GaN and the dashed line is that expected for a two-dimensional GaN layer biaxially strained to AlN (see text for details).

which considers the dot as a misfitting inclusion (GaN) in an infinite matrix (AlN). In order to describe the dot geometry, we have adopted a truncated cone shape with height 3 nm and base and top diameters equal to 13.3 and 3 nm, respectively, leading to an aspect ratio of 0.22. Furthermore, the dot is assumed to lie on a 0.5-nm-thick two-dimensional wetting layer. The output of the calculations is the full inhomogeneous strain tensor $\varepsilon_{ij}(\mathbf{r})$, from which the local strained values of a and c are obtained as $a(\mathbf{r})=[1+\varepsilon_{\rho\rho}(\mathbf{r})]a_0$ and $c(\mathbf{r})=[1+\varepsilon_{zz}(\mathbf{r})]c_0$, respectively. This procedure does not take into account the distortion caused by the shear strains, which are found to be very small throughout most of the dot volume. Figure 4 shows the distribution of a, c, and c/a values by means of two-dimensional contour plots in the ρ-z plane. In the wetting layer beneath the QD (z between −0.5 and 0 nm), the value of a tends to match that of relaxed AlN (3.112 Å). Whereas the QD is compressed in the plane, its c parameter expands over the value of relaxed GaN (5.185 Å). In this region the deformation is almost biaxial, i.e., as that of a thin two-dimensional GaN layer in a AlN matrix, where

$$\frac{c}{a}=\left(\frac{1+q\varepsilon_a}{1+\varepsilon_a}\right)\frac{c_0}{a_0},$$

$\varepsilon_a=-2.4\%$ being the in-plane misfit strain, and $q=-2C_{13}/C_{33}$, the Poisson ratio. Moving upward through the dot, the in-plane parameter increases, tending to (but never reaching) its relaxed GaN value. On the other hand, the c parameter decreases due to the influence of the AlN in which the QD is embedded, reaching first its relaxed value, and getting increasingly compressed toward the top surface of the QD. The result is that the value of c/a at the top surface is close to the relaxed value, but neither c nor a attain their unstrained values. In fact, for a taller QD, i.e., with a higher aspect ratio, a would be almost completely relaxed at the top surface, whereas c will be further compressed, tending toward the c value of relaxed AlN. Under these circumstances, the value of c/a might lie even below the value expected for the relaxed material.

To establish a closer connection between the theoretical results and the experimental values, we also display in Fig. 4(d) the theoretical depth profile of c/a extending from $z=-0.5$ nm (wetting layer underneath the QD) to $z=3$ nm (top of the QD). The values represented have been obtained by averaging the calculated c/a over the dot cross section perpendicular to the z axis. We can see that the experimental results shown in Fig. 3 are clearly enlightened by the calculations presented in Fig. 4(d). In the first place, we notice that the general trend of the measured gradient of c/a through the QD is well reproduced in the theoretical depth profile. As a matter of fact, the calculations establish that, inside the dot, the in-plane lattice parameter a is always compressed, although to different values depending on the position, whereas the parameter c is expanded in the base and compressed at the top of the dot. This interplay, which is very sensitive to the dot morphology and aspect ratio, results in a strain state quite inhomogeneous and distinct from the biaxial strain characteristic of two-dimensional films, which is frequently invoked to describe the deformation of self-assembled QDs. As far as the AlN/GaN interface is concerned, the calculated c/a value of 1.675 agrees very well with the experimental value for all samples. As concerns the GaN surface, on the other hand, the experiments reveal a smaller c/a value than predicted by the simulations. Nevertheless, the analysis of the theoretical deformation distributions performed above allows us to conclude that, at least for GaN QDs capped with AlN, the small values attained by c/a at the dot surface do not mean that dots are completely relaxed. Probably, the main reason for the discrepancies between experiment and theory is that, whereas measurements refer to uncapped GaN dots or GaN dots covered with a very thin layer of AlN, in the theoretical model the dot is assumed to be embedded in an infinite matrix. Also, the calculations presented here do not take into account the influence of neighboring dots. We have performed simulations (not shown here) for the case of a plane of dots and found that, although the presence of the nearby dots actually tends to approach c/a toward the biaxial value, this effect is of negligible magnitude for the dot density reported by the AFM measurements, in the present case.

It should also be noted that the details of the QD nucleation process can contribute to a local modification of the QD strain state as well as the one of the surrounding matrix. It has been demonstrated that the numerous threading edge dislocations present in AlN efficiently act as QD nucleation centers.[18] Then although the dots themselves are free of dislocations, the deformation of the surrounding AlN matrix may be modified by the presence of these threading edge dislocations. As a further source of discrepancies between calculations and experimental results, it might be noted that the detailed mechanism of GaN capping by AlN may play a role. Actually, it has been found that, in the first stages of capping, AlN wets the dots and exhibits a very rough surface. Next, a progressive smoothing of the surface has been observed by both *in situ* reflection high-energy electron diffraction (RHEED) measurements and high-resolution transmission electron microscopy. It might be recalled that, in the case of GaN/AlN bidimensional superlattices, it has been found that the elastic relaxation strongly depends on the roughness of the interfaces,[19] in relation to a dislocation formation mechanism implying the coalescence of GaN and AlN platelets. Although the situation is not yet clear, we suggest that in the case of GaN QDs capped with AlN, the intrinsic roughness of the GaN layer would possibly influence the AlN growth mode and/or strain relaxation.

In conclusion, it has been demonstrated that MEIS allows one to measure the deformation profile of semiconductor quantum dots with a depth resolution in the monolayer range. In the case of GaN quantum dots uncapped and capped by AlN layers, it has been found that dots experience a nonbiaxial strain. In agreement with the results of calculations performed in the framework of the elastic continuum theory, we conclude that they are partly relaxed, which results in the deformation of the surrounding AlN matrix. We have established that capping the GaN QDs with AlN induces a deep modification of the strain state: whereas 10 ML or 20 ML of AlN slightly affect the deformation profile in the lower part of the dots, this profile is clearly changed in the upper part of the dots.

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