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ABSTRACT

The bandgaps of short period ZnO/(Zn)MgO superlattices deposited on *c*-, *m*-, and *a*-ZnO substrates were examined both theoretically and experimentally. *Ab initio* calculations showed that the bandgaps of *c*-oriented polar superlattices are smaller than those of nonpolar ones; however, this is mainly due to different geometric configurations, because the influence of internal electric fields existing in polar superlattices is not very significant. The calculations revealed that for 5–6 MgO monolayers in the barriers, the bandgap values become independent of the barrier thickness, which suggests that such superlattices can be treated as sets of isolated ZnO wells. In the experimental part of this work, it is demonstrated that short period ZnO/MgO and ZnO/ZnMgO superlattices can be grown successfully on differently oriented crystalline bulk ZnO substrates using molecular beam epitaxy. The bandgaps of the superlattices were determined from low temperature photoluminescence measurements. It is shown that they agree well with the theoretical results.

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I. INTRODUCTION

Increasing scientific interest in group-II oxide semiconductors has been observed for the last few decades.^{1,2} Many of the interesting properties of oxides and the underlying physical mechanisms are under debate.

Oxides are often compared to nitrides. ZnO is in many respects similar to GaN. They both crystallize in the hexagonal wurtzite structure and have a similar, direct energy gap, E_g , of 3.35 eV. There are a few reasons why ZnO could be an interesting alternative or supplementary material for GaN. One of them is the fact that ZnO has a large exciton binding energy, 60 meV. It is expected that due to stable excitonic emission at room temperature, ZnO-based light emitters should be much brighter than GaN light emitters. Moreover, the ionicity of oxides is much higher than that in characterizing nitrides.

Due to different MgO and ZnO crystal structures (rocksalt and wurtzite), $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys have a tendency to be metastable. Phase segregation has been reported to occur in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ for $x > 33\%$ with a maximum energy gap of about 4.0 eV.^{3,4} To overcome this difficulty, an approach consisting of the use of $m\text{ZnO}/n\text{MgO}$ superlattices (SLs), where m and n represent the numbers of atomic monolayers (MLs), was proposed. Bandgap

engineering, crucial for the design of optoelectronic devices, can be realized in SLs by varying the layer thicknesses (m and n) and also by manipulating lattice geometry, which we can call geometrical lattice engineering. The proposed structures are also called quasi-ternary alloys or ordered alloys, like $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$.⁵ The first attempts to grow similar structures using ZnO and MgO bilayers were undertaken by Tanaka *et al.*,⁶ who fabricated ZnMgO quasi-ternary alloys by molecular beam epitaxy (MBE) on *a*-oriented sapphire substrates by sequential deposition of thin layers of ZnO and MgO. The reported bandgap values for 1ZnO/6MgO and 2ZnO/2MgO SLs will be compared with our calculated and measured gaps for $m\text{ZnO}/n\text{MgO}$ SLs.

In the next part of the paper, band structure calculations of binary $m\text{ZnO}/n\text{MgO}$ SLs and $m\text{ZnO}/n\text{Zn}_{1-x}\text{Mg}_x\text{O}$ SLs for $x = 0.33$ will be presented for several m and n values, as well as for different growth directions: polar-*c*, nonpolar-*m*, and nonpolar-*a*. The obtained bandgaps are compared with the bandgap values estimated in the experimental part of the paper from photoluminescence (PL) measurements performed on the set of $m\text{ZnO}/n\text{MgO}$ samples grown in the *c*- and *a*-direction and $m\text{ZnO}/n\text{Zn}_{1-x}\text{Mg}_x\text{O}$ samples with $x = 0.35 \pm 0.05$ grown in the *c*- and *m*-directions. Good agreement between theory and experiment is obtained.

II. METHODOLOGY

A. Experiment

Short period $m\text{ZnO}/n(\text{Zn})\text{MgO}$ SLs were grown by MBE on different ZnO substrates: ZnO/MgO SLs on *c*- and *a*-ZnO, whereas ZnO/ZnMgO multilayer structures on *c*- and *m*-ZnO. Our intention was to use two kinds of nonpolar substrates (*a*-ZnO and *m*-ZnO) for each type of structure, but due to problems with the availability of good quality ZnO substrates, we used *a*-ZnO for ZnO/MgO SLs and *m*-ZnO substrates for ZnO/ZnMgO SLs. However, it is known that ZnO-based layered structures grow in a similar way on both *a*-ZnO and *m*-ZnO substrates; therefore, using *m*-ZnO instead of *a*-ZnO does not significantly affect the expected results.⁷ Before growth, the ZnO substrates (from Crystal GmbH) were chemically cleaned and out-gassed in a buffer chamber at 700 °C. Then, the substrates were transferred to the growth chamber and annealed at 700 °C in oxygen flow. The standard growth procedure was to deposit first a 30 nm ZnO buffer layer, because MBE technology is essentially hydrogen-free, in contrast to hydrothermally grown bulk ZnO crystals. The lattice constants of MBE grown ZnO buffer layers and the substrates may differ, depending on doping, carrier concentration, and growth technique.⁸ All the multilayer structures were grown at 460 °C. Thin layers of ZnO, MgO, and/or ZnMgO were deposited sequentially and their thicknesses were estimated on the basis of growth conditions. Total thicknesses of SLs and average contents of Mg and Zn were determined using Rutherford Backscattering Spectrometry (RBS), a method perfectly suited for fast control of the elemental composition in such structures. However, the precise thickness values had to be determined using transmission electron microscopy (TEM). In the case of ZnO/ZnMgO, exact information on the barrier thickness was necessary for determining the Mg content in the barrier. The combination of TEM and RBS gives reliable verification of the data obtained on the basis of growth conditions. TEM was also used to study atomic ordering in the obtained structures. PL excited with 275 nm or 302.4 nm lines of an argon laser was measured to determine the SL bandgaps.

B. Theory

The band structures of the SLs were examined in a supercell geometry by self-consistent *ab initio* calculations based on the local density approximation (LDA) to the density functional theory. The values of total energies, atomic coordinates, and lattice parameters were determined by minimization of the Hellman-Feynman forces using pseudopotentials as implemented in the Vienna *ab initio* Simulation Package (VASP).⁹ A cutoff energy of 600 Ry for the plane wave basis set was sufficient to obtain converged results.

Subsequently, in the second step of calculations, the band structures were obtained with the Linear-Muffin-Tin-Orbital (LMTO)¹⁰ method in a full-potential version.¹¹ A semiempirical correction (LDA + C) was used to account for the deficiency of LDA in predicting semiconductor gaps.¹² The correction procedure (LDA + C) adds external potentials, which peak sharply at the nuclear sites and therefore produce an upward shift in the *s*-like conduction-band-minimum state

$$V(r) = V_0 \left(\frac{r_0}{r} \right) \exp \left[- \left(\frac{r}{r_0} \right)^2 \right]. \quad (1)$$

Here, V_0 and r_0 are adjustable parameters. The potential parameters are specific for the atomic species and therefore transferable in the sense that they can be determined for two binary compounds and subsequently be applied to systems where the compounds are combined, as in alloys, SLs, and heterojunctions. The parameters used in the present work were determined for MgO and ZnO separately by adjusting to experimental gap values and subsequently applied to the ZnMgO alloys and ZnO/(Zn)MgO SLs. They were kept unchanged, while the composition was varied. Our optimized values of the adjusting parameters were $V_0(\text{Zn}) = 1000$ Ry, $V_0(\text{Mg}) = 900$ Ry, $V_0(\text{O}) = 800$ Ry, at the atomic sites, with the range parameter set to $r_0 = 0.015$ a.u. for all atoms. At all empty spheres, we applied $V_0 = 0.70$ Ry and $r_0 = 0.60$ a.u.

III. ZnO/MgO SUPERLATTICES

The built-in electric fields in polar quantum structures reduce the overlap of the electron-hole wave functions and lower the related radiative recombination rates. This reduces the efficiency of optoelectronic devices. One way to reduce or even eliminate the internal electric field is to grow quantum-well structures and related emitters along the nonpolar-*m* and -*a* directions. The properties of SLs grown in different crystal directions will be compared below.

A. Growth and characterization of ZnO/MgO samples

The first sample, polar ZnO/MgO SL, was grown on a *c*-oriented ZnO substrate. A 30 nm ZnO buffer layer was deposited on the substrate as usual, and then a 30 nm ZnMgO buffer layer was grown to reduce the lattice misfit and to accommodate the strain between the substrate and the first MgO ML. The SL was composed of 80 pairs of ZnO/MgO layers, each nominally 0.5 nm thick (2/2 MLs) as estimated based on growth conditions. The total SL thickness was 80 nm. To check the real layer thicknesses, RBS and TEM imaging were used and the results have been presented in the paper by Stachowicz *et al.*¹³ RBS showed that the overall quality of the structure is very good, as χ_{min} —the minimum ratio of backscattering yield for aligned and random geometry—was 3% only. Simulations of the random spectrum using SIMRA code revealed that the average Mg content in the SL is ~48%, which suggests that the ZnO and MgO layer thicknesses are almost equal, as expected. It was also found from the simulations that the Mg content in the ZnMgO buffer layer was approximately 35%. The TEM imaging shows a layered structure; however, the layers are not atomically flat and reveal some wavy character.

The low temperature (from 10 to 200 K) PL spectra of the investigated *c*-ZnO/MgO sample excited with the 275 nm line of the Ar laser are presented in Fig. 1. The strong emission between 3 and 3.45 eV comes from the *c*-ZnO substrate. The dominant line in this part of the spectrum is the D^0X emission at 3.361 eV, which shifts with temperature by about 0.03 meV/K, following roughly the temperature changes of the ZnO bandgap.¹⁴

In the high energy part of the PL spectra, two broad bands can be distinguished, which behave with temperatures in a different way. The band peaking at 4.05 eV shifts anomalously with temperature toward lower energies and at 70 K is located already at 3.98 eV, 70 meV lower than at 10 K. Evidently, the shift of this band cannot

FIG. 1. Low temperature PL spectra of the 2ZnO/2MgO SL grown on c-ZnO.

be explained by temperature evolution of the bandgap. The anomalous temperature behavior, together with its width, allows us to assign the 4.05 band to nonuniformities in the SL structure, probably due to structural imperfections, such as local composition fluctuations near the interfaces, which are known to affect the line width significantly in the case of narrow quantum wells and high ZnMgO barriers.^{3,15} On the other hand, the peak at 4.22 eV is almost stable with the temperature regarding its peak position. The estimated temperature shift of this band is about 0.03–0.04 meV/K, i.e., similar to D^0X at 3.361 eV, and of the same order of magnitude as the temperature shift of the ZnO bandgap.¹⁴ The width of the 4.22 eV band can be again explained by structural imperfections. The full width at half maximum (FWHM) of the PL lines in ZnO/ZnMgO increases with increasing Mg content and with decreasing thickness of quantum wells (QWs). This is due to fluctuations of compositions at/near interfaces. Assuming that the peak at 4.22 eV corresponds to the excitonic transition in the SL, the bandgap energy should be approximately $4.22 + 0.06$ eV, where 0.06 eV is the binding energy of the exciton in bulk ZnO.

Figure 1 illustrates that the PL spectra of short period SLs reveal some features, which may be due to imperfections in the SL. The problem of anomalous temperature dependence of the PL peak assigned to SL imperfections deserves detailed discussion and its nature requires further studies.

The next two ZnO/MgO SLs were grown on a-ZnO substrates. They were composed of 30 pairs of 2.6/1 nm ZnO/MgO, which corresponds roughly to 10ZnO/4MgO SL, and 30 pairs of 2.5/1.7 nm ZnO/MgO, which corresponds to 10ZnO/6MgO. In Fig. 2, the PL spectra of both SLs are presented and it is seen that the PL is influenced mainly by the thickness of the MgO barrier, as the thicknesses of ZnO wells are in principle the same in both SLs. In the case of the 2.6/1 nm ZnO/MgO SL, the highest energy band is located at 3.47 eV. If we take into account the exciton binding energy, we can estimate the bandgap of this structure to be about

FIG. 2. Low temperature (10 K) PL spectra of the ZnO/MgO SLs grown on a-ZnO substrates.

3.5 eV. In the 2.5/1.7 nm ZnO/MgO SL, three PL bands are observed, with the highest energy band located at 3.52 eV ($E_g \approx 3.6$ eV).

B. Band structure calculations of ZnO/MgO SLs

In Fig. 3, energy bandgaps vs the number of barrier MLs, n , are presented for m ZnO/ n MgO SLs (short notation m/n) grown along polar c -direction (a), nonpolar a -direction (b), and nonpolar m -direction (c).

The obtained bandgaps for polar SLs can be compared with the values measured and calculated by Tanaka *et al.*⁶ Their results for 1/6 SL and 2/2 SL are indicated in Fig. 3(a) (green stars). The bandgaps obtained by them are lying significantly lower than our calculated bandgaps, especially their E_g for 2/2 SL (3.60 eV—measured, 3.66 eV—calculated) seems to be too small. The bandgap of short period SL with layer thickness of the order of one lattice constant (2 MLs) should be comparable, but slightly lower than that of a 50% random alloy, just like it is in the case of ordered $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ (Ref. 5) and $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ (Ref. 16) alloys. In our case, it should be close to E_g of the random $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$ alloy determined theoretically (~ 4.3 eV)¹⁷ and experimentally (~ 4.4 eV).¹⁸ In this context, our calculated value of the 2ZnO/2MgO SL bandgap (~ 4.2 eV) seems to be quite reasonable. Moreover, it is in agreement with the PL measurements. The red error bar in Fig. 3(a) corresponds to the PL emission energy + exciton binding energy ($4.22 + 0.06$ eV).

The calculated bandgaps for nonpolar- a m ZnO/ n MgO SLs can be compared with experimentally estimated E_g values for two 10ZnO/4MgO and 10ZnO/6MgO SLs. The experimental values are in a good agreement with the general trend, as it is shown in Fig. 3(b). Comparing the bandgap behavior of polar [Fig. 3(a)] and nonpolar [Figs. 3(b) and 3(c)] m ZnO/ n MgO SLs, we observe that the general trends are the same. The results of calculations suggest that MgO barriers with 6 MLs are already thick enough to treat the ZnO wells in the SLs as separate quantum wells,

FIG. 3. Bandgaps of $m\text{ZnO}/n\text{MgO}$ SLs as functions of the number of barrier MLs grown along the polar c -direction (a), the nonpolar a -direction (b), and the nonpolar m -direction (c) in comparison with experimental data, when available. Green stars are from Ref. 6 and red bars represent our experiment (see explanation in the text).

independent of their thickness. This theoretical result seems to be well confirmed by the experimental data.

The E_g values are slightly higher in nonpolar structures, reaching 5.5 eV for SLs with one ML QWs, as compared to about 5 eV in polar SLs. Usually, with an increasing number of QW MLs, m , E_g significantly decreases, whereas with an increasing number of quantum barrier (QB) MLs, n , E_g first increases and then (for $n = 5$ –6 MLs of MgO) saturates, becoming independent of n . The exceptions are polar SLs with QWs thicker than 3 MLs, where E_g first increases and then decreases with the number of QB MLs. We can connect this behavior to the influence of the built-in electric fields present in the polar-oriented structures.

C. Influence of the internal electric field

To estimate the influence of the internal electric field on the bandgap values in the polar case, we determine the change of the bandgaps, ΔE_g caused by the electric field

$$\Delta E_g = eE_w d_w, \quad (2)$$

where E_w is the strength of the electric field in QW and d_w is the

QW thickness. The electric fields in the wells of the $m\text{ZnO}/n\text{MgO}$ SL structures were estimated from the semimacroscopic model.¹⁹ Having determined ΔE_g , we compared the $m\text{ZnO}/n\text{MgO}$ bandgaps with the gaps, $E_g(\text{hyp})$ for the hypothetical case corresponding to the internal electric field “switched off,” i.e.,

$$E_g(\text{hyp}) = E_g(\text{SL}) - \Delta E_g, \quad (3)$$

where $E_g(\text{SL})$ is the SL bandgap. In Fig. 4, we present the bandgap dependence on barrier thickness for polar and nonpolar SLs with 1 ML QW thickness, i.e., $1\text{ZnO}/n\text{MgO}$ (a) and with 7 MLs QW, i.e., $7\text{ZnO}/n\text{MgO}$ (b). The calculated $E_g(\text{SL})$ for the polar case is compared with the estimated $E_g(\text{hyp})$ corresponding to the internal electric field “switched off.” Surprisingly, we observe that $E_g(\text{hyp})$ is lying quite close to $E_g(\text{SL})$, especially for SLs with single monolayer QW thickness [Fig. 4(a)]. This result is in contradiction to the common belief that the internal electric field strongly influences the bandgaps in polar-oriented SLs, as observed in the case of nitride SLs.²⁰ We connect the origin of small internal electric field values in ZnO/MgO SLs with partly compensated spontaneous and piezoelectric components of the polarization. In Fig. 4, we observe that the bandgap

FIG. 4. Bandgaps of $1\text{ZnO}/n\text{MgO}$ (a) and $7\text{ZnO}/n\text{MgO}$ (b) SLs as functions of the number of barrier MLs, n , grown along the polar c -direction, the nonpolar a -direction, and the nonpolar m -direction. The calculated $E_g(\text{SL})$ for the polar case are compared with the estimated $E_g(\text{hyp})$ (green dashed lines).

FIG. 5. Low temperature (10 K) PL measured on three samples of ZnO/ZnMgO: a 1 nm/1 nm structure grown on c-ZnO and 1 nm/1 nm and 1.6 nm/1.6 nm structures grown on *m*-ZnO.

values with the switched-off electric field, $E_g(hyp)$, keep the same trend as E_g obtained for nonpolar SLs, but still are lying significantly lower. It seems that the differences in the bandgap values between SLs grown along polar and nonpolar crystal directions are mostly due to the different atomic geometries. On the other hand, the change of the bandgap caused by the internal electric field is proportional to the QW thickness [Eq. (2)]. Consequently, although very small in the case of $m=1$ [Fig. 4(a)], in SLs with thicker QWs, it is more pronounced and can be responsible for the decrease of the bandgap energies for larger m and n values in polar ZnO/*n*MgO SLs [see Fig. 3(a)]. In Fig. 4(b), we observe this effect for $m=7$, where $E_g(hyp)$ does not decrease with QB thickness in contrast to the case of $E_g(SL)$.

IV. ZnO/ZnMgO SUPERLATTICES

Short period ZnO/ZnMgO SLs were grown on *c*- and *m*-plane ZnO. Each SL was composed of 50 pairs of ZnO well and

ZnMgO barrier layers. The average content of Mg in the barrier was determined by the RBS technique. In the polar case, the sample was 1 nm/1 nm with 40% Mg in the barrier, which corresponds to 4ZnO/4Zn_{0.6}Mg_{0.4}O SL. In the *m*-nonpolar case, two types of the SLs were prepared: 1/1 nm (35% of Mg) and 1.6/1.6 nm (30% of Mg). They correspond roughly to 4ZnO/4Zn_{0.65}Mg_{0.35}O SL and 7ZnO/7Zn_{0.7}Mg_{0.3}O SLs, respectively. The total thickness of the SLs was also confirmed by RBS. In Fig. 5, the low temperature PL spectra of these three SL structures are presented. As it is seen in Fig. 5, the peak positions of SLs deposited on *m*-ZnO differ, being equal to 3.736 eV and 3.557 eV for 1/1 nm and 1.6/1.6 nm SL, respectively.

The E_g values estimated from PL measurements are indicated in Fig. 6 in comparison with the results of theoretical calculations. In Fig. 6(a), the calculated bandgaps of polar mZnO/*n*Zn_{0.67}Mg_{0.33}O SLs for $m=1-5$ are presented as functions of the number of QB MLs, n . After analyzing the bandgap dependence on QB thickness, the increasing trend is observed for all the QW widths. We do not observe a decrease of E_g values for thicker QWs, as it was observed in the polar ZnO/MgO SLs [Fig. 3(a)]. It can be explained by even smaller values of the internal electric fields in ZnO/ZnMgO compared with ZnO/MgO SLs, due to the smaller QW-QB lattice mismatch. The experimental E_g value obtained from the PL measurements performed on the sample corresponding to polar 4ZnO/4Zn_{0.6}Mg_{0.4}O SL, estimated as PL emission energy + exciton binding energy, is indicated by the red error bar. We observe a good agreement with the calculated bandgap for the similar 4ZnO/4Zn_{0.67}Mg_{0.33}O structure.

In Fig. 6(b), the calculated bandgaps of mZnO/*n*Zn_{0.67}Mg_{0.33}O SLs grown in the nonpolar *m*-direction are presented. The E_g values estimated from PL measurements on *m*-oriented samples corresponding to 4ZnO/4Zn_{0.65}Mg_{0.35}O and 6ZnO/6Zn_{0.7}Mg_{0.3}O SLs are indicated by red bars. Again, the agreement between our experiment and calculations is quite good.

In both Figs. 6(a) and 6(b), we observe that the bandgap values do not reach the plateau, as it is in the case of binary ZnO/MgO SLs for more than 5–6 MLs (Fig. 3). The dependence of E_g on barrier thickness starts to saturate above 6–7 MLs barrier thickness. It can be explained by the different character of wave function hybridization in both cases. The hybridization between ZnO well and Zn_{0.65}Mg_{0.35}O barrier is weaker, but also

FIG. 6. Calculated bandgaps of mZnO/*n*Zn_{0.67}Mg_{0.33}O SLs grown along the polar *c*-axis (a) and the nonpolar *m*-axis (b), as functions of the number of barrier MLs. The experimentally estimated values are indicated by red bars (see explanation in the text).

it saturates more slowly with the barrier thickness than in the case of ZnO/MgO.

V. SUMMARY

The bandgaps of short period ZnO/MgO SLs (ordered alloys) grown on *c*- and *a*- oriented ZnO substrates and ZnO/Zn_{0.67}Mg_{0.33}O SLs grown on *c*- and *m*-ZnO have been examined using self-consistent *ab initio* calculations. It has been shown that the bandgaps for *c*-oriented SLs are smaller than for nonpolar-oriented SLs. However, the influence of internal electric fields in polar SL is rather small and the differences in the bandgap values are mainly due to different atomic geometries. The calculations also show that for 5–6 MgO MLs (7–8 MgZnO MLs) in the barrier (barrier thicknesses above 1.5–2 nm), the bandgap values become independent of the number of monolayers in the barriers, which suggests that the whole structure can be treated as a multilayer structure containing isolated ZnO wells. In the experimental part of our work, we demonstrate that short period ZnO/MgO and ZnO/ZnMgO SLs can be obtained using MBE on differently oriented crystalline bulk ZnO substrates. Good control of growth parameters allowed us to fabricate SLs with “well-defined” interfaces. The bandgaps of SLs were determined using low temperature PL measurements. Optical transitions were attributed to excitons localized in the ZnO wells. It is shown that the experimentally determined values of E_g generally agree well with the theoretical ones. It seems that intermixing during growth is negligible.

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