

There is a possible contribution from rotation of the crystallites, but the major contribution is the domain reorientation within the crystallites during poling because the activation energy of the domain reorientation is much lower than that of the rotation of the crystallites. For the saturation poling time, however, adhesion, mechanical bonding, space charge, and/or surface charge polarization at the polymer/ferroelectric interface could not be excluded. Therefore, more detailed work is needed to prove the above hypothesis.

IV. Summary

The 0-3 composites were prepared using a dielectric gel with 70 vol% loading of coprecipitated PbTiO_3 powders with sizes of 12 to 1100 nm and a very narrow particle size distribution. XRD of the composites before and after poling indicated that saturation poling was nearly achieved at $E = 80$ kV/cm, 85°C, for 15 min in these composites. \bar{d}_{33} decreased with decreasing particle size. Composites of fine PbTiO_3 powders needed much longer poling time than coarse powders (larger than 200 nm), probably because of rotation of the single-domain crystallites during poling.

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Effect of Residual Strain on the Electronic Structure of Alumina and Magnesia

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The reflectance spectra of polycrystalline Al_2O_3 and single-crystal MgO, with different surface treatments, were measured using vacuum ultraviolet (VUV) spectroscopy to determine the effect of residual stresses and strains. The bulk stresses were estimated using the *R*-line fluorescence of trace Cr^{3+} in Al_2O_3 . No grain-size dependence was observed for the residual thermal expansion anisotropy stresses in polycrystalline Al_2O_3 . The effects of mechanical-polishing-induced damage in Al_2O_3 shifted the band-to-band and exciton transitions to higher energies, compared with those of chemically polished Al_2O_3 . There was little difference in peak positions between cleaved and chemically polished surfaces of MgO. However, mechanically pol-

ished MgO surfaces exhibited band-to-band and exciton-peak shifts to higher energies. The VUV technique of determining the exciton-peak and band-gap shifts was used with knowledge of the band-gap strain coefficient to estimate the magnitudes of residual surface stresses in the 1- μm surface layer probed. The polishing-damage-induced residual surface stress is 2.2 GPa for Al_2O_3 and 1.1 GPa for MgO. These values are based on band-gap strain coefficients of 700 meV/(lin% strain) derived for Al_2O_3 and 400 meV/(lin% strain) estimated for MgO. [Key words: strain, alumina, magnesia, surface, reflectance.]

I. Introduction

RESIDUAL stresses in ceramics, which originate from a mismatch in strain among regions in the body, have been studied mainly because of their effects on mechanical properties. We have investigated the effects of residual bulk and surface stresses on the electronic structure of Al_2O_3 and MgO. These results have enabled us to use optical means to measure residual strains in ceramics.

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Three types of residual stresses were studied: (1) macrostress, (2) microstress, and (3) surface stress. Macro residual stresses arise because of an uneven temperature distribution within a compact during cooling. Micro residual stresses, or thermal expansion anisotropy (TEA) stresses, arise when the polycrystalline compact has an anisotropic thermal expansion coefficient; randomly oriented grains shrink by different amounts.¹ Although both macro- and microstresses are bulk stresses, the latter is an inhomogeneous stress since the sign of the stress changes between two adjacent grains, whereas the former is a homogeneous stress. Surface stress can be induced by various surface treatments, such as the mechanical polishing of this study, whereas chemical-polishing techniques produce relatively damage-free surfaces. Surface residual stresses are usually confined to a thin, damaged layer, for example, 1 and 50 μm for Al_2O_3 ² and MgO ,³ respectively, when samples are mechanically polished with diamond pastes.

II. Experimental Procedure

X-ray diffraction techniques⁴ have been the most widely used method to measure surface residual stresses. In Al_2O_3 , bulk residual stresses have also been measured using a spectroscopic (ruby *R*-line fluorescence) technique⁵ because of the presence of trace Cr^{3+} in the Al_2O_3 . Vacuum ultraviolet (VUV) spectroscopy in the band-gap region gave us a new technique, well suited to surface stress determination and fundamentally related to the strain dependence of the electronic structure.

The experimental arrangement for ruby *R*-line fluorescence consisted of an Ar laser (488 nm, 500 mW) as the light source, a cryogenic sample chamber, a monochromator,⁶ and a photomultiplier tube as the detector. Because the peak widths increased rapidly with the temperature above 80 K, all results were obtained with the samples immersed in liquid nitrogen. A Ne line ($6929.47 \times 10^{-1} \text{ nm}$) (6929.47 \AA) was introduced in the spectra to determine the absolute peak positions.

The ruby *R*-line technique produced a signal in the red, at which the absorption coefficient of Al_2O_3 was very low, and, therefore, supplied information from the bulk of the sample. It was well suited for determining bulk macro- and microstresses.

The VUV reflectance was measured from 7.5 to 15 eV (165 to 83 nm) in the band-gap region. However, spectroscopically, the shift of the absorption edge was difficult to determine because of variations in the magnitude of the reflectance; therefore, the shift of the exciton peak was determined and used to approximate the shift of the band gap. In previous studies of the temperature dependence of the electronic structure, the exciton peak was found to shift very closely with the absorption edges in both Al_2O_3 ⁶ and MgO .⁷ The details of the VUV system are described elsewhere.⁸

The absorption coefficient at the band gap is important in the determination of the penetration depth or sampling depth of VUV measurements. Although we have not determined the absorption coefficient for Al_2O_3 at this time, we have found that Al_2O_3 is a direct band-gap material.⁶ Typically, the absorption coefficient in the region of a direct band-gap transition is of the order of 10^4 cm^{-1} as is found for AgCl ⁹ or direct-gap semiconductors. Therefore, the penetration depth of the VUV light is on the order of 1 μm . These results are also consistent with the sampling depths we have observed by successive chemical polishing of the samples; we are able to experimentally observe polish-damage layers which have an extent of 1 μm . Because of this penetration depth, the VUV method is especially suited for measurement of the highly localized surface strain or stress arising from polishing or tempering. The reflectance of the bulk can be obtained only when the sample surface is prepared relatively free of surface damage.

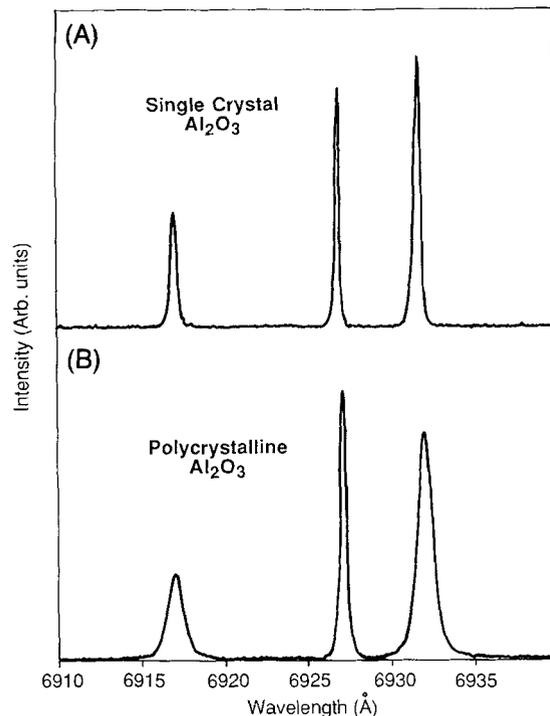


Fig. 1. Typical *R*-line fluorescence spectra of Al_2O_3 : (A) single-crystal and (B) polycrystalline Al_2O_3 .

(1) Al_2O_3

Polycrystalline Al_2O_3 samples with average grain sizes of 1, 10, and 100 μm were prepared using high-purity commercial Al_2O_3 powders.⁸ Disk-shaped compacts (diameter of 10 mm, thickness of 5 mm) were formed by pressing at 280 MPa (40 000 psi). The control of grain size was achieved by sintering the compacts at different temperatures (1450° to 1800°C) or doping them with 0.25 mol% MgO . The cooling rate used was 10°C/min except for the samples sintered at 1800°C, where the compacts were cooled at a rate of 100°C/min. In addition, one commercial-sintered Al_2O_3 ⁹ with an average grain size of 10 μm was used for comparison.

Surface stresses were induced by mechanically polishing a surface with diamond pastes (final grit size of 1 or 0.25 μm). To prepare a "damage-free" surface, samples were further polished using a colloidal silica (40-nm (400-Å) particle size).

(2) MgO

Three types of surfaces for MgO single crystals** were prepared: cleaved and mechanically and chemically polished. The layer of MgO damaged because of mechanical polishing with diamond pastes was removed by chemical polishing in hot phosphoric acid (100°C). For MgO , only VUV spectroscopy was used to observe the effect of surface treatments.

III. Results

(1) Al_2O_3

Typical *R*-line fluorescence spectra of single-crystal and polycrystalline Al_2O_3 are shown in Fig. 1. Macro- and microstresses of polycrystalline Al_2O_3 were calculated from the peak shift and broadening, respectively, assuming that the chemically polished single crystal was stress free. The TEA micro residual stress was expected to be a function of grain size for Al_2O_3 because of the lower "freezing" temperature, below which no stress relaxation could occur, and the faster creep relaxation rate with smaller grain size.¹⁰ Despite 2 orders of magnitude difference in grain sizes, no grain-size dependence was found for the microstresses as shown in Fig. 2. The single-crystal values in the figure represent the scattering of measurements. Fig. 2 also shows that the sample

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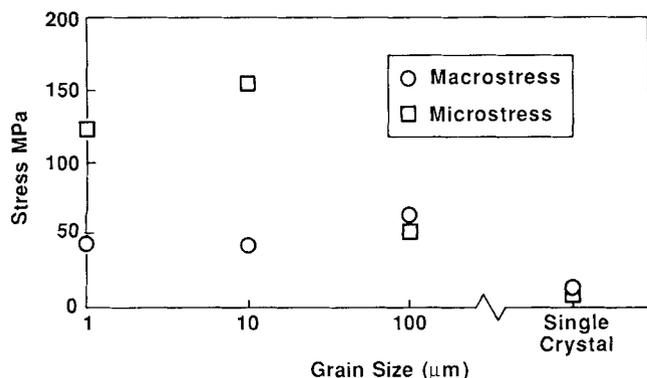


Fig. 2. Macro and micro residual stresses as a function of grain size for polycrystalline Al_2O_3 .

with a grain size of $100 \mu\text{m}$ has a reduced microstress, probably due to spontaneous microcracking.¹¹

Because of the absence of a grain-size dependence, the macro- and microstresses were averaged for all samples measured and were 50 and 135 MPa, respectively. Considering that residual stress is a function of various processing variables, these values are in good agreement with previous results.^{10,12}

We attempted to measure the bulk residual stress-induced shift of the band-gap and exciton features using VUV spectroscopy. Because of the inherent surface-layer sensitivity of band-gap spectroscopy, it was very important to prepare a surface which was free of polishing-induced damage so as to observe the bulk stress state. Figure 3 shows the reflectance spectra of a damage-free polycrystalline and single-crystal Al_2O_3 . The exciton peak was shifted 0.02 eV because of the effects of macrostresses. The broadening of the exciton peak, arising from the inhomogeneous microstresses, varied from sample to sample. Both of these measurements were at the resolution limit of the VUV spectrophotometer used.

Polishing-induced surface stresses were of much larger magnitude than the bulk residual stresses and produced much more dramatic VUV results. The VUV reflectance of an initially damage-free polycrystalline Al_2O_3 sample which was then mechanically polished is shown Fig. 4. Mechanical polishing induced exciton-peak shifts of 0.26 eV to higher energy. As stated earlier, peak 1 was observed to shift closely with the band gap, and, therefore, we found that the band gap of Al_2O_3 was increased 0.26 eV because of the damage induced by mechanical polishing.

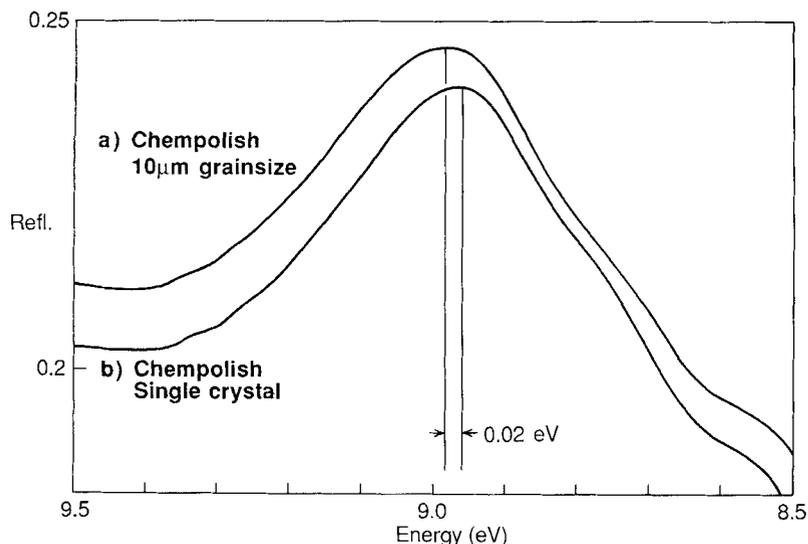


Fig. 3. VUV reflectance in the exciton-peak region for chemically polished single-crystal and polycrystalline Al_2O_3 , showing the effect of residual stresses.

This is shown in Fig. 5, where a damage-free single crystal is compared with various mechanically polished polycrystalline samples. Because we probed the band-gap region of the material, these results are intrinsic to Al_2O_3 and are unaffected by trace impurity contents, previous processing, or other factors. All mechanically polished samples exhibit identical peak shifts, also showing the 0.41-eV shift of the $13\text{-eV O } 2p$ to $13\text{-eV Al } 3p$ peak.

(2) MgO

The effect of surface treatments of MgO single crystals on VUV reflectance is shown in Fig. 6. A comparison of the exciton peaks (peak 1) of cleaved and chemically polished surfaces shows no difference in position. The damage by cleavage, which is limited to narrow slip bands, is too small to change the band gap. However, this damage can be detected at the higher energy peak (peak 2): peak 2 shifts 0.06 eV from 13.5 eV for the chemically polished surface to 13.56 eV for the cleaved surface. This negligible effect suggests that the cleavage method, which has been the standard sample preparation procedure for spectroscopic work, can be used for VUV spectroscopy of MgO. In addition, the cleaved surface is more environmentally stable compared with the chemically polished surface. The chemically polished surfaces, although they have no slip-band damage, are very reactive, quickly forming carbonates or hydroxides.

The mechanically polished surface shows a 0.16-eV shift of the band gap to higher energy. Successive chemical polishing shows the damage layer thickness to be $50 \mu\text{m}$, in agreement with previously reported results.³

IV. Discussion

(1) Al_2O_3

From the ruby *R*-line fluorescence measurements, we found no grain-size dependence for the TEA-induced microstresses in polycrystalline Al_2O_3 . The ruby *R*-line technique is a sensitive method for determining both the TEA bulk microstresses and the thermal-quenching-induced bulk macrostresses.

Our attempts to use these bulk stresses to calibrate the VUV band-gap spectroscopy were unsuccessful. The stress or strain dependence of the band gap is not large enough to be appreciably affected by the bulk residual stresses.

VUV band-gap spectroscopy is very sensitive to the mechanical-polishing-induced damage and its surface residual strain. In addition, because of the inherent $1\text{-}\mu\text{m}$ surface-layer sensitivity, it is well suited to studies of polishing-induced damage.

It is necessary to develop a calibration of the VUV exciton and band-gap shifts to relate the observed spectroscopic results to surface stresses and strains. An absolute calibration of the magnitudes of the polishing-induced surface stresses or strains can be determined from a first-principles determination of the strain depend-

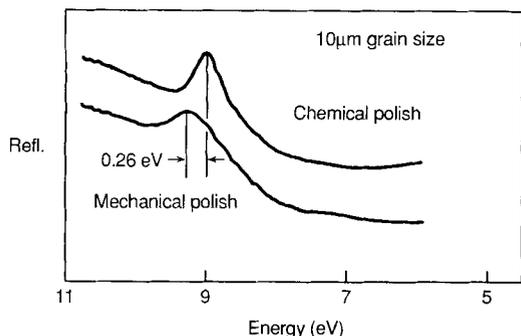


Fig. 4. VUV reflectance of mechanically and chemically polished polycrystalline Al_2O_3 showing the polishing-induced exciton-peak shift.

ence of the band gap. It is more appropriate to proceed in terms of the strain dependence, since the band gap is affected by strains which arise from either elastic stresses or plastic deformation.

The band gap, which is the energy between the nonbonding and antibonding orbitals of the valence and conduction band is a direct function of the interatomic spacing or bond length of a material. The strain dependence can be directly measured as the pressure dependence of the band gap, but, for Al_2O_3 , this is difficult since the band gap energy (8.8 eV) is not accessible in diamond anvil cell spectroscopic experiments, which are limited to energies below 6 eV. From previous experimental and theoretical studies of the temperature dependence and the associated effects of lattice thermal expansion on the electronic structure of Al_2O_3 ,⁶ we have determined the magnitude of the temperature-induced band-gap change and the relative contribution of the lattice expansion and the electron-phonon interaction (arising from atomic vibrations). We accurately determined the band-gap temperature dependence, and, using first-principles band structure techniques, we calculated the relative contributions of thermal expansion to the temperature dependence. We performed a first-principles density functional theory calculation of the effect of bond-length or lattice-parameter changes on the band gap. We found it to be linear up to 2 lin% strain. The band gap decreases with increasing bond length. Thermal expansion is responsible for 55% of the temperature dependence. The experimentally determined temperature dependence of the band gap is -1.1 meV/K, implying that lattice expansion is responsible for 0.6 meV/K. The lattice thermal expansion coefficient is $8.8 \times 10^{-6}/\text{K}$. These results allow us to calculate the strain dependence of the band gap to be 230 meV/(vol% strain) or, of more interest in the present case, the linear strain dependence of 700 meV/(lin% strain). We therefore have a direct relationship between the change in the band-gap energy and the local state of strain in the material. In addition, we know that an increase in the band-gap energy corresponds with a compressive strain in which the bond lengths are decreased.

It is important to address the fact that we simulated volumetric lattice dilatation, whereas we now apply the results to in-plane linear strains. In Al_2O_3 , the top of the valence band arises from O $2p$ states which are triply degenerate at $\mathbf{k} = 0$. In a calculation of volumetric dilatation, each of these bands will move identically since the symmetry is unbroken by pure volumetric dilation. We, therefore, calculate to first approximation the strain dependence of each of the degenerate O $2p$ bands, along with the other bands of the material. In the case of imposed surface strains, the degenerate O $2p$ bands will be split by the strain. Symmetry arguments predict that the split bands exhibit different optical activity, depending on the direction of the polarized light with respect to the strain field. These predictions have been found to agree fairly well with results for strain in semiconductors.¹³ In our VUV reflectance measurements, we will be independently measuring transitions from the optically allowed O $2p$ band, which is consistent with the polarization of the light, and probing the strain parallel to

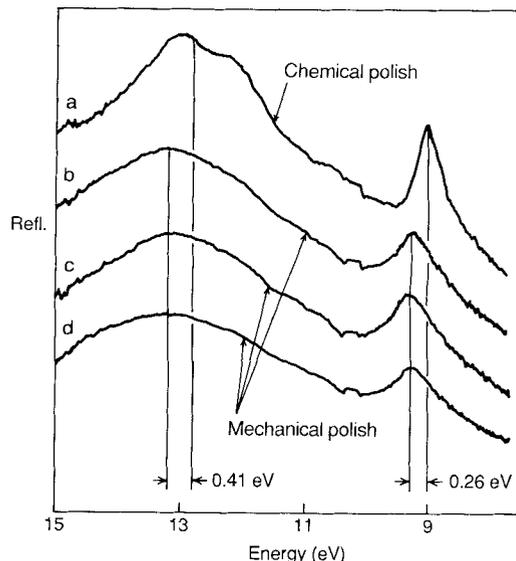


Fig. 5. VUV reflectance of (A) chemically polished single-crystal Al_2O_3 compared with various mechanically polished polycrystalline Al_2O_3 samples, demonstrating that the observed peak shifts are controlled by the polishing treatment and not the sample purity, origin, or processing. The polycrystalline samples are, respectively, (B) RHP DBM, 1- μm grain size, (C) Linde A, 10- μm grain size, and (D) Linde A, 100- μm grain size.

the polarization direction. Therefore, for a volume-conserving shear deformation, for example, we would observe different transition energies; in the tensile direction the energy would decrease, whereas in the compressive direction, the energy would increase. Since our calculation determined the strain or dilatation dependence of all three O $2p$ bands, the results are applicable to the present case where we observe the strain dependence of individual O $2p$ bands. Our VUV reflectance measurement is sensitive to in-plane strains and, to first order, is independent of the out-of-plane strains.

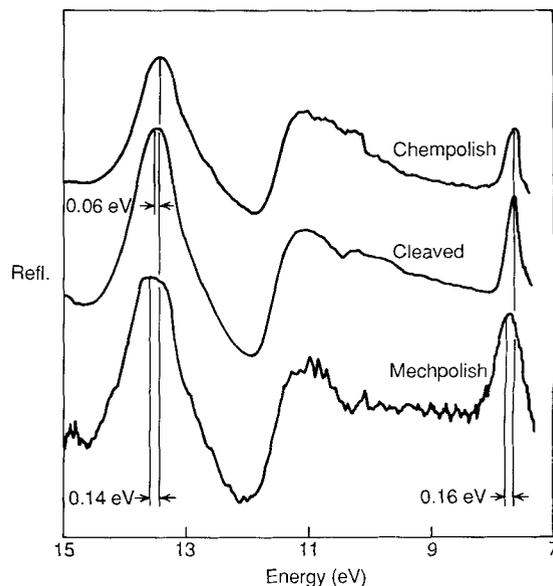


Fig. 6. VUV reflectance of single-crystal MgO for chemically polished, cleaved, and mechanically polished surfaces.

We can now discuss the actual magnitudes of the polishing-induced surface stresses in Al_2O_3 . With a band-gap strain coefficient of $700 \text{ meV}/(\text{lin}\% \text{ strain})$, the observed exciton-peak shift of 0.26 eV arising from mechanical polishing of Al_2O_3 corresponds to a linear in-plane strain of $-0.38 \text{ lin}\% \text{ strain}$. This compressive strain arises from the far-field stress distribution of the polishing-induced dislocations oriented with their dislocation line and Burgers vector parallel to the surface. This is an elastic strain, and the associated surface stress can be determined from the elastic constants. The biaxial nature of the stress requires that we take into consideration the Poisson effect. The surface stress is therefore -2.2 GPa in the $1\text{-}\mu\text{m}$ surface layer. The depth of the surface layer was confirmed to be $1 \mu\text{m}$ by successive chemical polishing. The tensile yield stress of Al_2O_3 is on the order of 600 MPa , whereas compressive yield stresses are typically an order of magnitude higher. Therefore, the polishing-induced surface stress reported here is reasonable in comparison with the compressive yield stress. Independent confirmation of our derived value of the band-gap strain coefficient would increase our confidence in the accuracy of these surface stress values.

The surface stress caused by grinding was reported¹⁴ to be much smaller (on the order of 100 MPa) in magnitude but extending to a significant depth ($<15 \mu\text{m}$) than the values we have found. This difference in the stress distribution for these two cases can be explained by the concept of line force, which is the product of the stress and the damaged-layer thickness. As empirically shown by Johnson-Walls *et al.*,¹⁵ the line forces, not the magnitude of the stress, are determined by the hardness of material. In the same material, therefore, the depth of damage is inversely proportional to the residual stress, which is the case for the difference between polishing and grinding damages.

(2) MgO

In single-crystal MgO, cleavage was found to cause only localized slip band damage and to produce relatively nonreactive surfaces, whereas chemical polishing produced damage-free surfaces, which were very reactive. For optical spectroscopy, where one averages over large regions of the surface, a cleaved surface is superior.

Mechanical polishing of MgO also produced dramatic changes in the VUV band-gap spectra, with the exciton, band-gap, and higher-lying transitions shifting to higher energies. The magnitudes of the shifts were smaller than those for Al_2O_3 . To calibrate these results in terms of the band-gap strain coefficient, we must know the band-gap temperature coefficient and the relative contribution of thermal expansion to the band-gap temperature dependence. From preliminary measurements,⁷ we have found that the band gap decreases at a rate of $1.0 \text{ meV}/\text{K}$. Assuming that the lattice expansion contribution to the band-gap temperature dependence for MgO is similar to that for Al_2O_3 , we can derive a value of $400 \text{ meV}/(\text{lin}\% \text{ strain})$. Therefore, the observed exciton shift of 0.14 eV corresponds to a compressive in-plane strain of $0.4 \text{ lin}\% \text{ strain}$, of the same order of magnitude as in Al_2O_3 . This polishing-induced strain penetrates 40 to $50 \mu\text{m}$ into the sample because of the reduced hardness of MgO relative to Al_2O_3 . Because of the elastic properties of MgO, this strain is caused by an elastic surface stress of -1.1 GPa .

V. Conclusion

It is shown that vacuum ultraviolet (VUV) spectroscopy can be used to measure surface stresses. If the band-gap strain coefficient (i.e., band-gap shift/strain) is known, the VUV measurements directly determine the absolute magnitude of surface stresses. The $1\text{-}\mu\text{m}$ penetration depth of VUV light at the band-gap energy is ideally suited to surface stress studies. Successive polishing allows the measurement of the surface stress layer thickness.

Residual surface stresses induced by mechanical polishing produce a large change in the band-gap electronic structure. The band-gap strain coefficient for Al_2O_3 is $700 \text{ meV}/(\text{lin}\% \text{ strain})$. The 0.26-eV increase in the band gap is therefore caused by a $0.4 \text{ lin}\% \text{ strain}$ and a surface-layer stress of 2.2 GPa .

Residual bulk stresses in sintered polycrystalline Al_2O_3 show no grain-size dependence for the size range from 1 to $100 \mu\text{m}$. The average macro- and microstresses are 50 and 135 MPa , respectively. These stresses result in only a small change in electronic structure.

The cleaved and chemically polished MgO single crystals have the same band gap, indicating negligible damage by cleavage. Mechanically polished samples show a 0.16-eV shift of band gap, which suggests a surface stress of 1.0 GPa .

Note Added in Proof. In further work on the effects of thermal lattice expansion and the electron-phonon interaction on the electronic structure of Al_2O_3 and MgO, we have calculated new estimates of the hydrostatic, or volumetric, band-gap strain coefficients to be 352 and $111 \text{ meV}/(\text{lin}\% \text{ strain})$, respectively. These quantities correspond to the hydrostatic deformation potential of the band gap. If the stress state in the polishing-damaged surface layer were purely hydrostatic, these would correspond to surface stresses of 4.3 and 3.45 GPa in Al_2O_3 and MgO. Since the stress in the surface layer is not purely hydrostatic, but consists of both hydrostatic and shear components, it is necessary to utilize both the hydrostatic and shear deformation potentials of the band gap in deriving surface stresses from the observed strain-induced electronic structure shifts. The shear deformation potentials appear, from electron-phonon modeling involving shear modes, to be of larger magnitude, with the result being that the stress state in the surface layer corresponds to lower stresses than derived using only hydrostatic deformation potentials. The determination of these band-gap strain coefficients does not affect the experimentally observed strain-induced band gap and exciton peak shifts, only the calculated magnitude of the stresses producing the observed shift. Independent experimental determination of both the hydrostatic and shear deformation potentials is being undertaken.

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