

LETTER TO THE EDITOR

Dislocation-induced birefringence in CaF_2 for lithography optics

A M Stoneham

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Received 21 February 2002

Published 12 April 2002

Online at stacks.iop.org/SST/17/L15**Abstract**

Internal strain fields due to dislocations will cause birefringence in crystals such as CaF_2 . This birefringence will exceed levels considered acceptable for 157 nm lithography unless essentially all dislocations can be eliminated.

Lithography is moving to shorter and shorter wavelengths in response to pressures towards semiconductor device miniaturization. This, in turn, is placing demands on materials for lithography optics, and driving a move from silica to CaF_2 . The move to CaF_2 has raised particular concerns relating to birefringence. There is an intrinsic component, which might be reduced by alloying with BaF_2 [1]. There is also stress-induced birefringence, where industry has 'invested substantial resources to control stress-induced birefringence to one part in 10^7 (or, equivalently, 1 nm/cm)' [1]. This letter quantifies the likely role of dislocations normally present in fluorite. It appears very unlikely that birefringence can be reduced to the 1 in 10^7 level unless dislocations are eliminated.

Of course, birefringence is just one of several reasons for wishing to eliminate dislocations. For example, because they are natural defects to grow, or move, or to spawn other defects under UV excitation [2]. Further, in $(\text{Ca}, \text{Ba})\text{F}_2$ alloys, the strain fields will bias the relative proportions of Ba and Ca close to dislocation cores, and this segregation may affect any delicate compositional balance aimed at eliminating intrinsic birefringence.

The random strains due to dislocations can be quantified, both theoretically and experimentally through spectroscopy [3, 4]. The key characteristics are the magnitude characterizing these strains, and the scale length over which these strain fields change significantly. The strain to which we refer is a linear combination of the components of the strain tensor, the precise combination chosen to match the problem under consideration. For dislocations, theory and experiment agree that the distribution of strain fields is roughly Gaussian, so a root mean square (rms) strain can be defined. The magnitude of the rms strain will depend on the density, Burgers vectors, orientations and spatial distribution of the dislocations. The quantitative orders of magnitude quoted below assume

randomly-oriented, randomly-distributed straight dislocations for illustrative purposes. For a random distribution of point defects, such as a dilute solution of BaF_2 in CaF_2 , the distribution of strain fields is not Gaussian, but roughly Lorentzian, and the rms strain diverges, although there are useful ways to characterize the range of values.

Dislocations will be present in a concentration which is expressed as L , the length of dislocation per unit volume. It is usually given in cm/cc (1 cm/cc is 10^4 m/m³). A reasonably typical value for ionic solids is 10^5 cm/cc [5]. For this value, the rms strain is of order 10^{-4} . Roughly speaking, one expects an rms strain of order $3 \times 10^{-7} (L \text{ cm/cc})^{1/2}$. The piezooptic constants linking the strain tensor to the birefringence are of order unity for CaF_2 (see, e.g. [6]), that is to say, the birefringence will also have a distribution with rms value of order $3 \times 10^{-7} (L \text{ cm/cc})^{1/2}$. These estimates show that the root mean square birefringence will only be less than the acceptable average value of 10^{-7} for dislocation densities which are essentially zero.

As presented, this argument is too simple, since it does not mention a scale length. After all, in a simple silica glass, the variations in bond angles and lengths will certainly have rms values of effective strain which are reasonable large, but they have little effect optically because the scale lengths (not much larger than an atomic spacing) are much smaller than the wavelength of light. Even the density fluctuations in glasses (such as those which give Rayleigh scatter in optical fibres) have a scale length much less than the optical wavelength [7]. For a strictly random alloy (and $(\text{Ca}, \text{Ba})\text{F}_2$ might be an example, in the absence of dislocations or grain boundaries), the scale length will be a few interatomic spacings, unless the alloy is very dilute. For dislocations, the relevant scale length is roughly δ , the spacing of dislocations, or $1/L^{1/2}$. This is easily understood physically, and can also be derived formally

from the distribution of strain gradients. For the 'typical' ionic, with an L of 10^5 cm/cc, this is about 30μ , i.e., about 20 wavelengths of 157 nm light. For smaller dislocation densities, the scale length is even larger.

One expects the dislocation-induced stresses to create some regions with positive birefringence and others with negative values, i.e. there will be cancellations for any optical path. Since we are assuming a random distribution of dislocations, does this compensation eliminate the problem? For an optical system with a very short scale length, like the ideal random alloy, the answer is probably yes. For dislocations, a more careful analysis is needed. Suppose the optical component has thickness D . The path will encounter about $N = D/\delta$ dislocations *en route* through the component. The average spacing of dislocations δ is of order $L^{-0.5}$. For a component with thickness $D = 0.01$ m, we have roughly $N \sim L^{0.5}$, with L in cm/cc. Compensation by the sign fluctuations in the strain (and consequently in the birefringence) will effectively reduce the strain we should consider from the rms value by a factor of about $N^{1/2}$ or $L^{0.25}$. Thus, for $L \sim 10^5$ cm/cc the 10^{-4} birefringence is reduced by just over a factor 10 to 10^{-5} . This value is still much higher than the figures of 10^{-7} being cited as acceptable. For the very lowest dislocation densities, of course (e.g. $L \sim 1$ cm/cc), the precise dislocation structure must be considered, as dislocations running parallel to the surface will have different effects from those running normal to it.

In strictly random alloys, the fluctuations in interatomic distances can be quantified and, for a (non-dilute) random alloy, will change on a characteristic length scale of a few interatomic spacings [4, 8]. However, real alloy systems, like (Ca, Ba)F₂, are not strictly random. As mentioned, there can be strain-induced segregation close to dislocations which will affect birefringence. Further, there will be alloy fluctuations. In glassy systems, the analogous problem would be density

fluctuations. In fused silica glass [9] inhomogeneities of order 10^{-4} are reported level, leading to levels of residual stress of 31 nm/cm and wavefront distortion of above 90 ppm.

It would seem that dislocation-induced birefringence should be taken seriously in CaF₂ for lithography optics. This is especially so if (Ca, Ba)F₂ is to be used. It will be difficult to reduce this component of birefringence to acceptable levels without eliminating dislocations almost completely. There may be further problems associated with UV-induced defect processes causing property changes with time.

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