byssus collagen (6), short pepsin-solubilized peptides were sequenced by Edman degradation, and thus the presence of hydroxyproline in Y positions was demonstrated. Similar information exists for the annelid collagens but not for the mini-collagens. The byssus collagen contains many potential sites for Oglycosylation (for example, at Ser and Thr), but no information on their use exists. For an annelid cuticle collagen, a glycosylation of threonines in the Y position was demon-

strated (10), and these residues may substitute for the normally occurring hydroxyprolines. By analogy with the mammalian collagens it may be assumed that some noncollagenous domains of invertebrate collagens may be removed by enzymatic processing, but this information has to be provided by future work.

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**OPTICAL MATERIALS** 

# Light-Induced Anisotropy in Amorphous Chalcogenides

## Kazunobu Tanaka

Are all glasses isotropic? In general, the answer is yes because isotropic structure is one of the definitions of a glassy material. However, for one very interesting and unusual class of materials—the chalcogenides, a group of sulfur, selenium, and tellurium compounds—the molecular structure turns out to be strongly anisotro-

pic. This is because chalcogen atoms like sulfur or selenium are twofold coordinated in a random network of covalent bonds. Exposure of these materials to linearly or circularly polarized light produces a net anisotropy of the dielectric tensor, which results in optical anisotropy called dichroism and birefringence (see figure). In this way, polarization-dependent optical absorption and refraction can be induced in originally isotropic chalcogenide glasses (1). But now on page 1800 of this issue, Krecmer et al. (2) report an anisotropic mechanical effect induced by polarized light: Contraction occurs along the direction of the electric field vector of the inducing light, whereas dilatation occurs perpendicular to that direction. The result provides not only insight into the

underlying physics of anisotropic effects but also a technological potential for amorphous chalcogenides.

The optical axis of the induced anisotropy switches from one to the other in response to a change of the polarization direction of the inducing light. According to the results of the experiment of Krecmer *et al.*, which was carried out with a multilayer atomic force microscope (AFM) microcantilever including a layer of thin amorphous AsSe film, the light-induced optical anisotropy is al-



Scalar and vector effects in chalcogenide glasses. In a simplified twodimensional model, (**A**) all transition dipoles are randomly distributed after the exposure to unpolarized light (*z*-axis incidence), although isotropic photodarkening and photoexpansion occur (scalar effects). (**B**) Subsequent exposure to linearly polarized light along the *y* axis causes selective conversion of the transition dipoles directed along the *y* axis into the *x* axis, producing optical and mechanical anisotropy (vector effects): directional change in optical absorption (dichroism) and refractive index (birefringence). At the same time, directional compressive stress induces nanocontraction and nanodilatation along the *y* and *x* axes, respectively. (**C**) A change of the polarization direction of the inducing light from the *y* to the *x* direction rotates every anisotropy by a right angle.

ways accompanied by a mechanical anisotropy in terms of directional compressive stress. Actually, the microcantilever bends upward or downward depending on the polarization direction of the inducing light; there is a direct correlation between optical and mechanical anisotropy. Technologically, this experiment presents the possibility of a new kind of positioning device for nanotechnology, which can be controlled solely by polarized light. vol. 2, pp. 22–67.

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Noncrystalline chalcogenide semiconductors-including melt-quenched glasses and amorphous thin-film structures of Se, As<sub>2</sub>S<sub>3</sub>, or AsSe-exhibit a variety of optical and structural changes when exposed to light or other radiation that excites electron-hole pairs (3). Before the initial report on optical anisotropy by Zhdanov et al. (1), other wellknown light-induced phenomena, such as photostructural changes accompanying photodarkening, have been observed by many groups, although anisotropy was not seen. Optical anisotropic changes are, therefore, often called vector effects in order to distinguish them from photostructural changes and photodarkening, which are called scalar effects. Vector and

> scalar effects often take place in the same material under the same excitation but are completely different in nature (4). All of these light-induced effects are metastable and can be reversed by thermal annealing below the glass transition temperature, at which materials become supercooled liquid; the effects are unique to the amorphous phase and do not occur in its crystalline counterpart.

> Why are chalcogenide glasses so sensitive to band-gap light? And what is the microscopic origin of light-induced anisotropy? The most characteristic feature common to chalcogenide glasses is the electronic structure originated in *p*-like lone pair (LP) electrons of chalcogen atoms. Selenium has four outer *p* electrons, two of which

form two covalent bonds with *p* electrons from the neighboring two atoms and the remaining two of which are localized on the chalcogen atom as LP electrons. The LP electrons are energetically higher than bonding-state electrons and therefore occupy the top of the valence band. The presence of those high-energy LP electrons and the resultant low coordination number of the chalcogen atoms yields optical and

The author is at the Joint Research Center for Atom Technology National Institute for Advanced Interdisciplinary Research, Tsukuba-shi, Ibaraki 305, Japan. Email: tanaka@jrcat.or.jp

PERSPECTIVES

structural anisotropy on the molecular scale as well as a large flexibility in local bonding rearrangement in a disordered network. If we consider the chalcogenide glass as a randomly connected microvolume, each of which carries an independent anisotropic microstructure, polarized light can preferentially excite microvolumes having their optical axes along the electric field of the light. Thus, as has been pointed out by Fritzsche (4), a net anisotropy of the system can be realized only when hole-electron pairs recombine nonradiatively in their excited microvolumes, whereby some atomic rearrangements occur and rotate optical axes of some of the excited microvolumes. Occurrence of excitation and nonradiative recombination in the same microvolume is essential to the existence of vector effects, whereas diffusion of excited carriers out of microvolumes results in scalar effects, be-

#### APPLIED PHYSICS

# mes results in scalar effects, be- changes its middle-range order or sometimes PHYSICS Organic Solid-State Lasers:

### A. Dodabalapur, E. A. Chandross, M. Berggren, R. E. Slusher

**Past and Future** 

A world-wide race is on to achieve electrically pumped lasing in organic materials. Organic solid-state lasers have the potential to provide a compact, low-cost optical source over a broad range of wavelengths throughout the visible spectrum. Organic solid-state lasers are also an excellent example of how basic research in one area can influence many other fields, including some of considerable technological significance. Demonstrations of light amplification and laser action in photoexcited solid-state organic materials (1) rapidly followed the invention of liquid dye lasers (2). Since then, the results of organic laser research have had a substantial impact on many aspects of laser physics. The ability to define phase gratings holographically in organic materials made possible the first demonstrations of distributed feedback (DFB) and distributed Bragg reflector (DBR) lasers (3, 4) (see figure). These lasers had gain media consisting of a polymer host such as poly(methyl methacrylate) or gelatin doped with rhodamine 6G as a film on a glass substrate. Gratings that function as wavelength-selective mirrors are placed at the ends of the cavity in DBR lasers. The cavity

The authors are at Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974, USA. E-mail: ananth@physics.bell-labs.com and gratings are part of a waveguide that confines light along the plane of the active material. Upon photoexcitation, some of the light emitted is amplified in the cavity, and the mode that has the highest net gain becomes the lasing mode above threshold.

cause carriers lose the memory of preferen-

light-induced optical and structural anisot-

ropy, several structural models have been

proposed, but they are still controversial.

Many of them emphasize isolated short-

range atomic events such as bond switching

(5), modification of defects (6), or LP orbit-

als, whereas Lee et al. (7) and Tanaka et al.

(8) have suggested more cooperative and

longer range structural modification of the

network. Krecmer's result favors the latter.

Furthermore, quite recently, it has been re-

ported that chalcogenide glasses behave like

liquids in their local structure under photo-

excitation with respect to scalar effects (9).

This result suggests that a disordered net-

work of chalcogenide glasses is considerably

dynamic under photoexcitation and possibly

Regarding more detailed mechanisms for

tially excited microvolumes.

The successful realization of DBR and DFB lasers with dye-doped polymers was followed by efforts to replicate these resonator



Schematic structures of the first DFB (top) and DBR (bottom) lasers. In the DFB laser, feedback is provided throughout the gain region by a phase grating that was defined in the gelatin by intersecting ultraviolet beams. In the DBR laser, the gratings are defined at the ends of the laser cavity. [Adapted from (3, 4)]

long-range order through the cooperative effect of local atomic events.

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designs with III-V semiconductors such as GaAs, but success was slow to come because of processing difficulties. Eventually these difficulties were overcome, and both photopumped (5) and electrically driven DFB (6) lasers were demonstrated. Subsequent advances led to the widespread use of InP-based DFB and DBR lasers in long-haul optical communication systems. These lasers are favored because of their superior singlefrequency operation and high-speed modulation characteristics compared to conventional Fabry-Perot lasers.

Research on organic gain media—liquid and solid—was useful in clarifying many aspects of the operation of vertical-cavity surface-emitting lasers (VCSELs). For example, work with organic lasers improved understanding of the influence of the spontaneous emission factor  $\beta$  on the threshold characteristics of planar microcavity lasers (7, 8), which are similar to VCSELs. The factor  $\beta$  is the fraction of the total spontaneous emission that is coupled to the lasing mode below threshold. Microlasers with  $\beta$ close to 1 can have very low thresholds. The VCSELs based on III-V semiconductors are technologically important because of the compact volume, low-threshold currents, and high coupling efficiency to single-mode optical fibers.

Fluorescent organic dyes have been used to study the properties of spherical and nearspherical resonators (9). The lasing modes of such resonators are called "whispering gallery" modes or morphology-dependent resonances and are the optical analogs of acoustic whispering galleries that are found in buildings such as St. Paul's Cathedral in London. Experimental work on lasing in liquid droplets containing laser dyes (9) led to re-