CUDOS

The Centre for Ultrahigh bandwidth Devices for Optical Systems (CUDOS)

ANNUAL REPORT

2006

Professor Barry Luther-Davies

Barry Luther-Davies is a Federation Fellow and Professor of Laser Physics at the Australian National University with 36 years research experience in diverse areas such as lasers, laser-matter interaction physics, photonics, optical materials and nonlinear optics. He completed a BSc in Electronics and PhD in Laser Physics from the University of Southampton, UK.

Barry is a Fellow of the Australian Institute of Physics, the Optical Society of America and the Australian Academy for Technological Sciences and Engineering. He was awarded the Pawsey Medal of the Australian Academy of Science in 1986 for his contribution to laser-plasma interaction physics. He is currently a topical editor for the Journal of the Optical Society of America-B.

Key areas of research contribution within the Centre

Barry oversees the Centre's work at ANU fabricating planar optical waveguide devices and photonic crystals in chalcogenide glasses and is also science leader of the CUDOS flagship project Compact Optical Switch in 2-D Photonic Crystal which combines the skills of researchers at ANU, The University of Sydney and the University of Technology Sydney. His broad experience, which contributes to all aspects of the CUDOS projects, spans materials science; film deposition and patterning; optical characterization; and device design.

Roles and responsibilities within Centre

Group Leader: Laser Physics Centre, RSPhysSE, ANU;

Science Leader: Compact Optical Switch in 2-D Photonic Crystal.

Key areas of research activity: Research into properties of new chalcogenide glasses; thin chalcogenide film production by pulsed laser ablation; film processing for waveguide and photonic crystals; device and materials testing.

Research achievements during 2006

Nonlinear Materials and Planar Structures

Team: Barry Luther-Davies, Dukyong Choi, Steve Madden, Congji Zha, Rongping Wang, Andrei Rode, Eugene Gamaly, Douglas Bulla, Ruth Jarvis, Maryla Krolikowska, Anita Smith, Darren Freeman, Amrita Prasad.

Overview: Our program underpins CUDOS-wide efforts to demonstrate high performance all-optical processors exploiting the third order nonlinearity of chalcogenide glasses. Our research includes the fabrication of novel glasses; studies of their basic physical and optical properties; film production and characterization; and film processing to create low loss optical waveguides and photonic crystals. Structures are supplied to the flagship projects "Chalcogenide Integrated Circuits" and "Compact Optical Switch".

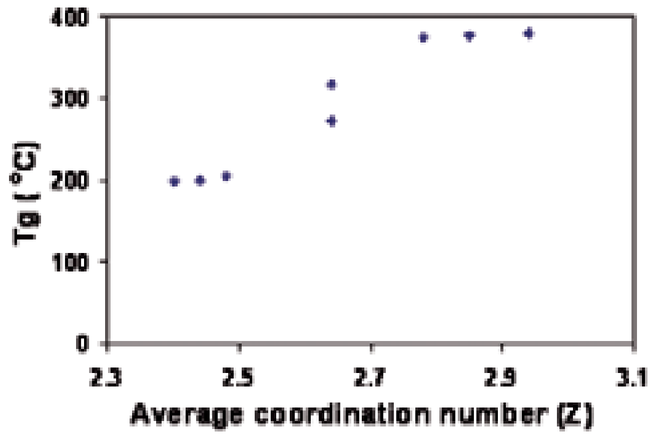
Bulk chalcogenide glasses and their properties

Chalcogenide glasses comprise a wide range of amorphous materials containing the chalcogen elements S, Se and Te compounded with network forming elements such as As, Ge, Si, etc. We have chosen these materials because they have high refractive index, large third order nonlinearity, and good photosensitivity whilst being free of absorption across the whole of the near- and mid-infra-red. A challenge with chalcogenides arises from their relatively weak chemical bonding. This results in low melting temperatures and structural instability, leading to a range of exotic phenomena such as quasi-crystallization and enhanced photosensitivity even at wavelengths well beyond their band edge.

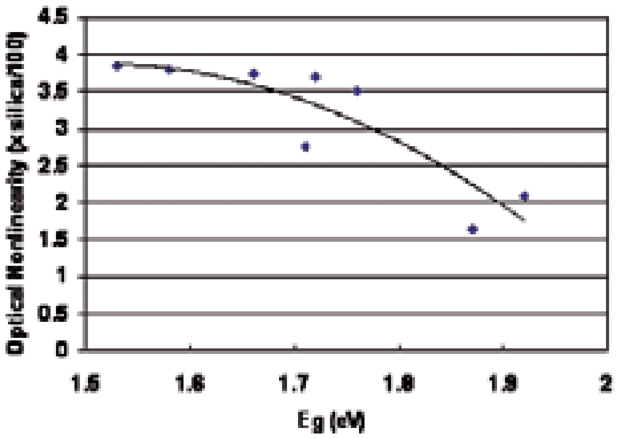
To identify glasses with a favourable combination of nonlinearity, absorption loss, glass transition temperature Tg and stability we study Ge-As-Se glasses with the focus being to better understand the composition-property relationships. Whilst glasses can be formed over a wide range of different compositions, high Ge or As content result in higher glass transition temperature (Tg) because of the increase in the mean coordination number which results in the glasses undergoing a transition from a "floppy" to "rigid" glass phase. The range of useful compositions may also be limited by factors such as phase separation.

By analyzing Raman spectra, the optical band gap and glass transition temperature (Tg) we have obtained a better understanding of how the glass structure evolves as the Ge content is increased from 0 to 39%. Raman data, which identify the dominant bonds present in the glasses, show that at low Ge content the glasses have a characteristic layer structure dominated by the presence of pyramids of $AsSe_{3/2}$ and $GeSe_{3/2}$. This leads to low values of glass transition temperature around 200 C and low values of the mean coordination number. As the Ge content increases, the glass develops a more three dimensional network dominated by Ge-Se bonds. By plotting glass transition temperature (Tg) values as a function of the mean co-ordinate number (Z) we have been able to identify a distinct structural transition to a 3D network connected by [$GeSe_{4/2}$] tetrahedrons that occurs at a critical value of $Z \approx 2.67$ (see Figure 1). Above this value the glass transition temperature jumps significantly to around 350 °C.

We have developed a new approach to the standard Z-scan technique for determining the third order optical nonlinearity of our glass samples that largely eliminates errors introduced by limited sample quality in these high index materials. For Ge-As-Se glasses over a wide range of compositions we have found that the third order nonlinearity is well predicted by the theory introduced by Sheik-Bahae et al which predicts that the highest nonlinearity occurs for wavelengths close to half the band gap of the material. As a result the relationship between composition and band gap is of paramount importance. We have shown that in the case of glasses containing 33% Ge, which includes the commercial glass AMTIR-1 ($Ge_{33}As_{12}Se_{55}$), the band gap can be tuned by adjusting the As and Se content. The AMTIR-1 composition lies in a region where phase separation should occur and its band gap – 1.89 eV – is significantly higher than ideal for optimal nonlinearity at 1550 nm (≈1.6 eV). AMTIR-1 nonlinearity is therefore, moderate at 200x silica. By increasing the As content to 27% the band edge shifts down to 1.65 eV and the glass moves into a composition range where phase separation should not occur and the nonlinearity increases (see Figure 2).



▲ **Figure 1. Variation of the glass transition temperature, Tg, as a function of average coordination number for Ge-As-Se glasses.**



▲ **Figure 2. Third order optical nonlinearity as a function of band gap for a wide range of Ge-As-Se glasses.**

As a result of this work we are in a better position to predict glass properties prior to fabrication for Z values where the 3-D network is properly developed. By ensuring we work outside the region where phase separation occurs, glasses with low optical loss combined with high nonlinearity and glass transition temperature appear feasible.

Relevant Publications and Presentations

[1] Zha C, Wang RP, Smith A, Prasad A, Jarvis RA, Luther-Davies B, Optical Properties and Structural Correlations of GeAsSe Chalcogenide Glasses, JOURNAL OF MATERIALS SCIENCE: MATERIALS IN ELECTRONICS (in press)

[2] Wang RP, Zha CJ, Rode AV, Madden SJ, Luther-Davies B, Thermal characterisation of Ge-As-Se glasses by differential scanning calorimetry, JOURNAL OF MATERIALS SCIENCE: MATERIALS IN ELECTRONICS (in press)

[3] Zha CJ, Luther-Davies B, Wang RP, Smith A, Prasad A, Jarvis RA, Madden S, Rode A, Optical Characterization of Ge-As-Se Glasses Containing High Content of Germanium, ACOFT, Melbourne, Australia (2006)

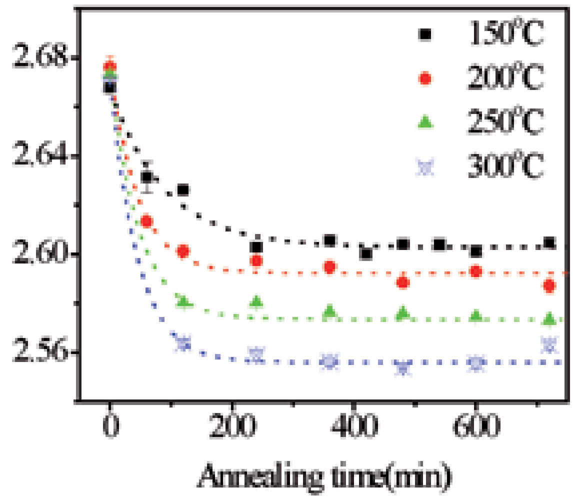
[4] Wang RP, Zha CJ, Rode AV, Madden SJ, Luther-Davies B, Thermal characterisation of Ge-As-Se glasses by the differential scanning calorimetry, International Conference on Optical, Optoelectronic and Electro-Optic Properties of Materials and Applications, Darwin, Australia (2006)

Film properties and processing

We use a special ultrafast pulsed laser deposition (UFPLD) system to produce high quality films for waveguide fabrication. However, in common with most physical vapour deposition methods for depositing chalcogenide films, UFPLD produces films with distinctly different bond structure from the bulk glass because of the non-equilibrium deposition from the vapour phase. The usual approach to correct this of depositing films onto hot substrates proved to be impractical with chalcogenides because of crystallization or large changes in the stoichiometry of the films. Thermal processing post deposition to anneal As_2S_3 films deposited at room temperature into a bulk-like state also produced crystallization in the As_2S_3 thin films.

This year we made similar annealing studies of AMTIR-1 films but used X-ray Photoelectron Spectroscopy (XPS) to diagnose the bond structure at the film surface. A SCI Filmtek wafer mapper was also used to measure refractive index and thickness while the films were annealed. We found that prolonged annealing at high temperatures (300 °C for >3 hours) relaxed the glass towards a refractive index matching the bulk (see Figure 3) without the appearance of crystal peaks in the Raman spectra. Using XPS we could show that as-deposited material contained a large number of separated Se clusters which coalesce with As and Ge after annealing at high temperatures thereby forming a matrix similar to that of the bulk glass. However, both Ge and As 3d XPS spectra show the presence of oxides. While thermal annealing seems effective in moving the film towards the bond structure of the bulk glass, the simultaneous surface oxidation must be suppressed to achieve high quality films. Recent studies by annealing under high vacuum suggest this is possible.

Since thermal annealing has proven effective in changing the bond structure of the chalcogenide films towards the bulk state, we investigated ion assisted deposition (IAD) to see if a similar result could be achieved. We added a Kaufmann and Robinson E400F ion gun to the deposition chamber to bombard the substrate with Ar+ ions during deposition. We did not see significant differences in the structure of films produced by IAD in Raman spectroscopy, but by ion cleaning the substrates prior to deposition we have achieved a large improvement in film adhesion that assists substantially during film processing.



▲ **Figure 3. Evolution of the refractive index of AMTIR-1 films annealed at different temperatures. The index of bulk glass is around 2.54.**

Relevant Publications and Presentations

[1] Wang RP, Madden SJ, Zha CJ, Rode AV, Luther-Davies B, Annealing induced phase transformations in amorphous As_2S_3 films, JOURNAL OF APPLIED PHYSICS 100, 063524 (2006)

[2] Choi D-Y, Madden S, Wang RP, Rode A, Krolikowska M, Luther-Davies B, Nano-phase separation of arsenic trisulphide (As_2S_3) film and its effect on plasma etching, JOURNAL OF NONCRYSTALLINE SOLIDS (in press)

[3] Wang RP, Rode AV, Madden SJ, Zha CJ, Jarvis RA, Luther-Davies B, Structural relaxation and optical properties of amorphous $Ge_{33}As_{12}Se_{55}$ films, JOURNAL OF NONCRYSTALLINE SOLIDS (in press)

[4] Wang RP, Zha C, Choi D, Luther-Davies B, Madden S, Rode A, Impact of Annealing Temperature on As_2S_3 Films Produced by Ultra Fast Pulsed Laser Deposition, Amercian Ceramics Society, Glass and Optical Materials Annual Meeting, Greenville SC (2006)

Device fabrication

Chalcogenide all-optical devices operating at sub-W powers require waveguides with small mode areas to increase the intensity. As the waveguide dimensions shrink the fabrication challenges rise because surface roughness has a larger and larger impact on waveguide losses. During 2006 we carried out an extensive study of the origin and control of roughness on plasma etched As_2S_3 surfaces.

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) images indicate that As_2S_3 surfaces etched with our standard CF_4-O_2 plasma process have a characteristic nanoscale grainy structure (see Figure 4a). From Raman scattering and surface-sensitive XPS studies, we have concluded that this grainy morphology comes from the differential chemical attack rates between As-rich and S-rich phases in the as-deposited films. Evidence for differential attack comes from XPS data showing that after etching the content of As atoms in As-As bonds increased from 17% to 32% whilst S atoms in S-S bonds dropped from 17% to 11%.

Two approaches were found to be effective for improving the smoothness of etched surface: a change of the plasma chemistry from CF_4-O_2 to CHF_3-O_2 (Figure 4b); and the application of a conformal thin As_2S_3 coating onto a structure already patterned using CF_4-O_2 plasma (Figure 4c). In both these cases the surface roughness was significantly reduced from around 3 nm RMS to ≈1.5 nm RMS and was accompanied by an increase in correlation length of the roughness. Our calculations indicated that the optical losses should be reduced by around a factor of 3 with this level of reduced roughness.

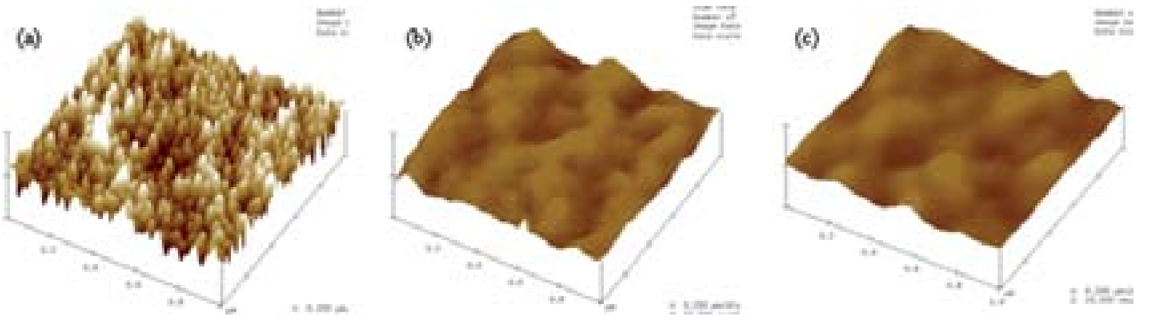
Some chalcogenides such as As_2S_3 are subject to film attack by standard photo-resist developers. We successfully developed two new approaches for protecting the As_2S_3 surface from attack. The first involves coating a thin (≈50nm) layer of a more robust glass, currently AMTIR-1, on top of the As_2S_3 prior to processing. The second involves using developer-resistant back AR coating (BARC) as a protective film ≈200 nm thick below the photo-resist (see Figure 5). After development of the photo-resist the BARC is removed by oxygen plasma prior to etching the chalcogenide in CHF_3-O_2 plasma.

Using CHF_3-O_2 plasma we etched rib waveguides into 1.75 μm thick AMTIR-1 films deposited by UFPLD onto oxidized Si wafers. Measurements of the insertion and polarization dependent loss (PDL) were made using the cut-back method for guides with different rib widths from 3 to 6 μm. Losses were around 0.27 dB/cm – the lowest ever reported for AMTIR-1. A number of interesting trends emerged. The polarization dependent loss (PDL) varied widely as a function of guide width being as small as 0.25 dB for 3 μm wide guides but jumped to >20 dB for 4 μm guides. By examining the polarization state of radiation emerging from the waveguides we found that large PDL is associated with coupling of the fundamental mode to a leaky mode of opposite polarization. The origin of this coupling is unclear although film birefringence is likely to play a significant role.

We also observed that as-deposited AMTIR-1 films displayed significant reversible photo-induced loss when exposed to low-level visible light. The origin of this effect is unclear but is likely associated with the presence of Se clusters (discussed above) in as-deposited films. However, we have so far been unable to observe photoconductivity in film samples exposed to light. The bulk glass shows no evidence of photo-induced loss at moderate light intensities.

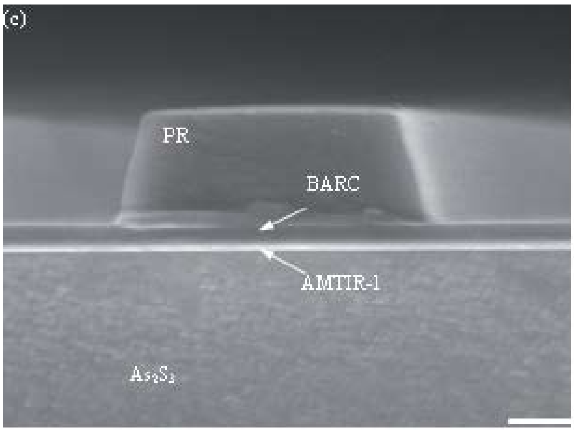
We developed a new approach for producing high performance sampled Bragg gratings (SBG) in chaclogenide waveguides. This provides a platform for wavelength division multiplexed (WDM) on-chip signal processing in a compact integrated device. SBGs are produced by using an amplitude mask to spatially modulate a Bragg grating written holographically into the core of the waveguide. Since any physical separation between the mask and waveguide will compromise the grating's spectral characteristics, we patterned the shadow mask directly on top of the waveguide cladding to create periodic pairs of openings through which the grating writing beams enter to interfere in the waveguide and create the grating.

We coated an As_2S_3 rib waveguide with a 21±0.02 μm thick layer of spin-on inorganic polymer glass ™ . The mask was formed by patterning a 1 μm layer of AMTIR-1 which is opaque at the grating writing wavelength of 532 nm, but has advantages over the use of an Al mask in as much as inhibits multiple reflections between the

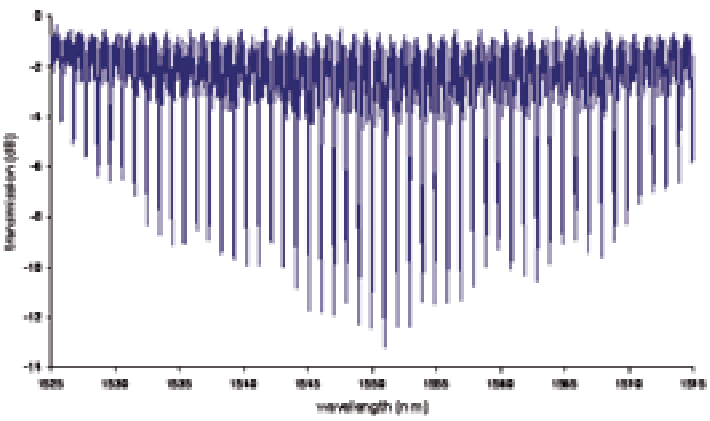


▲ **Figure 4. (a) AFM image of surface of As_2S_3 etched in CF_4-O_2; (b) AFM image of surface of As_2S_3 etched in CHF_3-O_2 showing improved surface quality; (c) AFM image of surface (a) after recoating with 150nm As_2S_3 layer.**

Si substrate and the mask layer. This shadow mask allowed SBGs to be written uniformly over the whole wafer producing the sharpest response so far reported for any material (see Figure 6).



▲ **Figure 5. SEM image of patterned photoresist on top of a BARC and AMTIR-1 coated As_2S_3 film that act as protective layers during resist development.**



▲ **Figure 6. The spectral response of a SBG written into an As_2S_3 waveguide.**

Photonic crystals

We produce photonic crystals by milling chalcogenide films deposited onto thin Si_3N_4 membranes with a focused ion beam (FIB). To cancel any mechanical or electronic drift that occurs during the lengthy milling process, we have developed custom hardware and software to monitor and eliminate such drift. This was successfully applied to the production of photonic crystal waveguides and micro-resonators during 2006, described elsewhere in this report, and is currently being applied to the production of photonic crystal hetero-structures aimed at obtaining higher Q cavities than are currently available. Metal films were FIB-patterned as part of a collaboration with a team at the University of Melbourne working on metamaterials and plasmonics. A lengthy machine breakdown hampered progress in the latter part of the year.

Relevant Publications and Presentations

[1] Choi DY, Madden S, Rode A, Wang R, Luther-Davies B, Fabrication and optical Characterisation of $Ge_{33}As_{12}Se_{55}$ (AMTIR-1) Thin Film Waveguides, IEEE LEOS, Montreal (2006)

[2] Madden S, Choi D, Rode A, Luther-Davies B, Low Loss Etched $Ge_{33}As_{12}Se_{55}$ Chalcogenide Waveguides, ACOFT, Melbourne (2006)

[3] Choi DY, Madden S, Rode A, Wangh R, Luther-Davies B, Advanced processing methods for As_2S_3 waveguide fabrication, IEEE Conference on Optoelectronic and Microelectronic Materials and Devices, Perth (2006)

[4] Freeman D, Luther-Davies B, Madden S, Real time drift correction of a focused ion beam milling system, International Conference on Nanoscience and Nanotechnology, Brisbane (2006)

[5] Freeman D, Luther-Davies B, Madden S, Real time drift correction of a focused ion beam milling system, NSTI Nanotechnology Conference, Boston (2006)

[6] Freeman D, Luther-Davies B, Grillet C, Madden S, Rode A, Krolikowska M, Chalcogenide glass photonic crystal membranes fabricated by focused ion beam milling, International Conference on Nanoscience and Nanotechnology, Brisbane (2006)

[7] Freeman D, Luther-Davies B, Madden S, Stowe S, Drift correction of a focused ion beam for nano-fabrication of photonic crystals, 16th International Microscopy Congress, Sapporo, Japan (2006)

[8] Freeman D, Luther-Davies B, Madden S, Stowe S, Real-time drift correction of a focused ion beam milling system, 19th Aust. Conf. Microscopy and Microanalysis, Sydney (2006)

[9] Orbons SM, Freeman D, Gibson BC, Huntington ST, Luther-Davies B, Jamieson DN, Roberts A, Optical Properties of Nanoscale Annular Array Metamaterials, SPIE Optics and Photonics, San Diego (2006)

[10] Orbons S, Freeman D, Luther-Davies B, Gibson B, Huntington S, Jamieson D, Roberts A, Nanophotonic metamaterials, Aust. Inst. Phys. Congress, Brisbane (2006)

[11] Orbons SM, Freeman D, Luther-Davies B, Gibson BC, Huntington ST, Jamieson DN, Roberts A, Nanoscale annular array metamaterials, International Conference on Nanoscience and Nanotechnology, Brisbane (2006)

[12] Orbons SM, Freeman D, Luther-Davies B, Gibson BC, Huntington ST, Jamieson DN, Roberts A, Optical Properties of silver composite metamaterials, ETOPIM, Sydney (2006)

Laser-induced micro-explosions in bulk materials

Team: E. Gamaly, A. Rode, B. Luther-Davies (with collaborators in Japan S. Juodkazis, K. Nishimura, S. Tanaka, H. Misawa; and France: Hallo, P. Nicolai, and V. T. Tikhonchuk).

In collaboration with researchers in Japan (Misawa, Juodkazis, Nisjimura, Tanaka) and France (Tikhonchuk, Halo, Nicolai) we have continued theoretical and joint experimental work on micro-explosions and photo-modification of materials by intense laser pulses focused inside bulk transparent solids. This year we reported experiments on photo-structuring of As_2S_3 bulk glass using intense fs pulses; the production of extreme conditions within a laser induced micro-explosion - equivalent to those existing in a nuclear explosion; and void formation in silica and sapphire. This work relates closely to studies at Swinburne University involving photonic crystal fabrication via void formation inside transparent dielectrics.

Relevant Publications and Presentations

[1] Juodkazis S, Kondo T, Misawa H, Rode A, Samoc M, Luther-Davies B, Photo-structuring of As_2S_3 glass by femtosecond irradiation, OPTICS EXPRESS 14, 7751-7756 (2006)

[2] Juodkazis S, Nishimura K, Tanaka S, Misawa H, Gamaly EG, Luther-Davies B, Hallo L, Nicolai P, Tikhonchuk VT, Laser-induced microexplosion confined in the bulk of a sapphire crystal: evidence of multimegabar pressures, PHYSICAL REVIEW LETTERS 96, 166101, (2006)

[3] Gamaly EG, Juodkazis S, Nishimura K, Misawa H, Luther-Davies B, Hallo L, Nicolai P, Tikhonchuk VT, Laser-matter interaction in the bulk of a transparent solid: Confined microexplosion and void formation, PHYSICAL REVIEW B: CONDENSED MATTER AND MATERIALS PHYSICS 73, 214101 (2006)

[4] Juodkazis S, Misawa H, Hashimoto T, Gamaly E, Luther-Davies B, Laser-induced microexplosion confined in a bulk of silica. Formation of nanovoids, APPLIED PHYSICS LETTERS 88, 201909/1-3 (2006)

[5] Gamaly EG, Luther-Davies B, Rode AV, Laser-matter interaction confined inside the bulk of a transparent solid, Eds. H. Misawa and S. Juodkazis, WILEI-VCH, Weinheim, 5-36, (2006)

[6] Gamaly E, Rode AV, Luther-Davies B, Ultra fast Laser Ablation and Film Deposition, in Pulsed Laser Deposition of Thin Films, R. Eason Ed., John Wiley & Sons, Hoboken, New Jersey, 99-130 (2006)

[7] Gamaly EG, Uteza OP, Rode AV, Samoc M, Luther-Davies B, Non-equilibrium transformations of solids induced by femtosecond laser: Coherent displacement of atoms, SPIE – International Conference on Laser Ablation, Taos, New Mexico USA (2006)

[8] Gamaly EG, Madsen NR, Rode AV, Kolev VZ, Luther-Davies B, Effects of non-equilibrium energy distribution of surface atoms on the onset and rate of laser ablation: experiments and theory, SPIE – International Conference on Laser Ablation, Taos, New Mexico USA (2006)

[9] Gamaly EG, Joudkazis S, Misawa H, Luther-Davies B, Rode A, Hallo L, Nicolai P, Tikhonchuk VT, Laser-induced micro-explosion inside of sapphire crystal: Evidence of Multi-Megabar pressure, XXIX European Conference on Laser Interaction with Matter, Madrid, Spain (2006)