letters to nature

- Eisenberg, H. S., Silberberg, Y., Morandotti, R., Boyd, A. R. & Aitchison, J. S. Discrete spatial optical solitons in waveguide arrays. *Phys. Rev. Lett.* 81, 3383–3386 (1998).
- Fleischer, J. W., Segev, M., Efremidis, N. K. & Christodoulides, D. N. Observation of two-dimensional discrete solitons in optically induced nonlinear photonic lattices. *Nature* 422, 147–150 (2003).
- Sato, M., Hubbard, B. E., Sievers, A. J., Ilic, B. & Craighead, H. G. Optical manipulation of intrinsic localized vibrational energy in cantilever arrays. *Europhys. Lett.* 66, 318–323 (2004).
- Swanson, B. I. et al. Observation of intrinsically localized modes in a discrete low dimensional material. Phys. Rev. Lett. 82, 3288–3291 (1999).
- Fehske, H., Kinateder, M., Wellein, G. & Bishop, A. R. Quantum lattice effects in mixed-valence transition-metal chain complexes. *Phys. Rev. B* 63, 245121 (2001).
- Schwarz, U. T., English, L. Q. & Sievers, A. J. Experimental generation and observation of intrinsic localized spin wave modes in an antiferromagnet. *Phys. Rev. Lett.* 83, 223–227 (1999).
- Xie, A., van der Meer, L., Hoff, W. & Austin, R. H. Long-lived Amide I vibrational modes in myoglobin. *Phys. Rev. Lett.* 84, 5435–5438 (2000).
- Markovich, T., Polturak, E., Bossy, J. & Farhi, E. Observation of a new excitation in bcc He-4 by inelastic neutron scattering. *Phys. Rev. Lett.* 88, 195301 (2002).
- Chikamatsu, M., Tanaka, M. & Yamazaki, H. Effect of magnetic dipolar interaction on antiferromagnetic resonance in (C₁H₂NH₂)₂CuCl., *I. Phys. Soc. Jpn* **50**, 2876–2883 (1981).
- de Jongh, L. J. in *Physics and Chemistry of Materials with Low-Dimensional Structures* (ed. Lévy, F.)
 Statematic Chemistry of Materials and Chemistry of Computer Science (Computer Science)
- Sato, M., English, L. Q., Hubbard, B. E. & Sievers, A. J. Influence of sample shape on the production of intrinsic localized modes in an antiferromagnetic lattice. J. Appl. Phys. 91, 8676–8678 (2002).
- English, L. Q. Studies of Intrinsic Localized Spin-Wave Modes in Antiferromagnetic Crystals. Ph.D. thesis, Cornell Univ. (2003).
- Rössler, T. & Page, J. B. Intrinsic localized modes in driven anharmonic lattices with realistic potentials. *Phys. Lett. A* 204, 418–426 (1995).
- Sato, M. et al. Observation of locked intrinsic localized vibrational modes in a micromechanical oscillator array. Phys. Rev. Lett. 90, 044102 (2003).
- 22. Shen, Y. R. The Principles of Nonlinear Optics (John Wiley & Sons, New York, 1984).
- Almeida, N. S. & Mills, D. L. Nonlinear infrared response of antiferromagnets. *Phys. Rev. B* 36, 2015–2023 (1987).
- Lim, S.-C., Osman, J. & Tilley, D. R. Calculation of nonlinear magnetic susceptibility tensors for a uniaxial antiferromagnet. J. Phys. D 33, 2899–2910 (2000).
- Lai, R. & Sievers, A. J. Identification of an intrinsic localized spin wave resonance in antiferromagnetic chains with single-ion easy-plane anisotropy. *Phys. Rev. B* 55, 11937–11940 (1997).

Acknowledgements We acknowledge conversations with P. Brouwer, L. English, B. Hubbard, D. Mills, J. Page, J. Parpia, J. Sethna and R. Silsbee. This work was supported by NSF-DMR and by the Cornell Center for Materials Research.

Competing interests statement The authors declare that they have no competing financial interests.

Correspondence and requests for materials should be addressed to A.J.S. (sievers@ccmr.cornell.edu).

Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors

Kenji Nomura¹, Hiromichi Ohta¹, Akihiro Takagi², Toshio Kamiya^{1,2}, Masahiro Hirano¹ & Hideo Hosono^{1,2,3}

¹ERATO-SORST, JST, in Frontier Collaborative Research Center, Mail Box S2-13, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

 ²Materials and Structures Laboratory, Mail Box R3-1, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan
 ³Frontier Collaborative Research Center, Mail Box S2-13, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

Transparent electronic devices formed on flexible substrates are expected to meet emerging technological demands where siliconbased electronics cannot provide a solution. Examples of active flexible applications include paper displays and wearable computers¹. So far, mainly flexible devices based on hydrogenated amorphous silicon (a-Si:H)²⁻⁵ and organic semiconductors^{2,6-10} have been investigated. However, the performance of these devices has been insufficient for use as transistors in practical computers and current-driven organic light-emitting diode displays. Fabricating high-performance devices is challenging, owing to a trade-off between processing temperature and device performance. Here, we propose to solve this problem by using a novel semiconducting material—namely, a transparent amorphous oxide semiconductor from the In-Ga-Zn-O system (a-IGZO)—for the active channel in transparent thin-film transistors (TTFTs). The a-IGZO is deposited on polyethylene terephthalate at room temperature and exhibits Hall effect mobilities exceeding $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is an order of magnitude larger than for hydrogenated amorphous silicon. TTFTs fabricated on polyethylene terephthalate sheets exhibit saturation mobilities of 6–9 cm² V⁻¹ s⁻¹, and device characteristics are stable during repetitive bending of the TTFT sheet.

Thin-film transistors (TFTs) are fundamental building blocks for state-of-the-art microelectronics, such as flat-panel displays and system-on-glass^{11,12}. Furthermore, the fabrication of low-temperature TFTs will allow flexible large-area electronic devices to be developed. These devices are flexible, lightweight, shock resistant and potentially affordable—properties that are necessary for large, economic, high-resolution displays, wearable computers and paper displays¹. Further, when combined with 'transparent circuit technology'^{13–17}, TFTs can integrate display functions even on the windscreens of cars.

Organic semiconductors and hydrogenated amorphous silicon (a-Si:H) have been extensively investigated for flexible electronics, and have demonstrated the ability to be fabricated into flexible solar cells and TFTs²⁻¹⁰. However, device performance is limited by the low mobilities of the channel materials (field effect mobilities, μ_{FE} , are $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a -Si:H, $\sim 2.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a pentacene single crystal, and $\sim 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a pentacene thin film¹⁰). In addition, Si-based devices are of less interest for transparent circuits because they are not transparent, owing to the small bandgap¹⁸.

Amorphous semiconductors are preferred over polycrystalline ones for active layers from the viewpoints of processing temperature and uniformity of device characteristics. However, the carrier mobility of a-Si:H is lower by two or three orders of magnitude than that of single-crystalline Si ($\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for carrier concentration $\sim 10^{19} \text{ cm}^{-3}$). The mobility of a-Si:H is limited to $\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, as carrier transport is controlled by hopping between localized tail-states and band conduction is not achieved. The low mobility is associated with the intrinsic nature of the chemical bonding (Fig. 1a): average carrier transport paths in covalent semiconductors such as a-Si:H consist of sp^3 orbitals with strong directivity and, therefore, the bond angle fluctuation significantly alters the electronic levels, leading to somewhat high-density deep tail-states.

In contrast, degenerate band conduction and large mobility $(>10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ are possible in amorphous oxide semiconductors (AOSs) containing post-transition-metal cations^{19,20}. These features are completely different from those of the covalent semiconductors. Figure 1b illustrates the carrier transport paths (that is, the wavefunction of the conduction band bottom) in AOSs. The bottom of the conduction band in the oxide semiconductors that has high ionicity is primarily composed of spatially spread metal ns orbitals with isotropic shape (here n is the principal quantum number), and direct overlap among the neighbouring metal ns orbitals is possible. The magnitude of this overlap is insensitive to distorted metal-oxygen-metal (M-O-M) chemical bonds that intrinsically exist in amorphous materials^{21,22}. Therefore, AOSs exhibit Hall-effect mobilities similar to those of the corresponding crystalline phase, even if they are formed at room temperature. These carrier transport properties are unique to oxide semiconductors, and are not seen in covalent amorphous semiconductors such as a-Si:H.

Here we report room-temperature fabrication and performance of flexible TTFTs fabricated using a-IGZO as an active n-channel layer. Films of a-IGZO were prepared by pulsed laser deposition with a KrF excimer laser, using a polycrystalline InGaZnO₄ target at room temperature in an oxygen atmosphere (oxygen pressure P_{O_2}). The chemical composition of the obtained films measured by X-ray fluorescence spectroscopy was In:Ga:Zn = 1.1:1.1:0.9 (in atomic ratio).

Figure 2a shows an X-ray diffraction pattern of an a-IGZO film deposited on a glass substrate. The film is amorphous and optically transparent in the entire visible and near-infrared regions (wavelength $\lambda = 390-3,200$ nm), as shown in Fig. 2a inset. The optical transmittance is greater than 80%, including the reflection associated with the film and glass substrate. The optical bandgap (E_g) estimated from the Tauc' plot is ~3.0 eV, which is similar to that of the crystalline phase (~3.4 eV). The electrical conductivities at room temperature are $<10^{-5}$ S cm⁻¹ when the films are deposited at $P_{O_2} > 6$ Pa. The values correspond to carrier concentrations of $<10^{14}$ cm⁻³ if an electron mobility of 1 cm⁻² V⁻¹ s⁻¹ is assumed. The sign of the Seebeck coefficients obtained from thermopower measurements is negative, indicating that a-IGZO is an n-type semiconductor.

Figure 2b shows the room-temperature Hall mobility of a-IGZO films as a function of carrier concentration. This carrier concentration varies from $<10^{14}$ to 10^{20} cm⁻³ when P_{O_2} is varied from ~7 to 0.1 Pa. The data obtained on single-crystalline InGaO₃(ZnO)₅ (c-IGZO) films are shown for comparison. We have reported²³ that carrier transport in c-IGZO is governed by percolation conduction over the distribution of potential barriers around the conduction

band edge; these potential barriers are formed owing to random distribution of Ga^{3+} and Zn^{2+} ions in the crystal structure. The potential barriers are overcome when carrier concentration exceeds $3 \times 10^{18} \text{ cm}^{-3}$, and therefore the Hall mobility increases as the carrier concentration increases, and larger Hall mobilities (>10 cm² V⁻¹ s⁻¹) are obtained at carrier concentrations >10¹⁸ cm⁻³. Similar behaviours are also observed in a-IGZO, which would result from a similar mechanism associated with the random amorphous structure.

The amorphous phase is thermally stable up to \sim 500 °C in air. Other AOSs such as a-ITO, and also crystalline ZnO (an amorphous phase of ZnO has yet been reported), have high-density carriers even in as-deposited states, and are difficult to make into devices with controlled characteristics. Thus it is vital to choose a material in which carrier concentration can be controlled at a low level, for example, $<10^{14}$ cm⁻³, in order to achieve a low off current and large on-to-off current ratios²⁴. Incorporating Ga ions would be important in a-IGZO for suppressing carrier generation via oxygen vacancy formation, because the Ga ion forms stronger chemical bonds with oxygen than Zn and In ions.

We fabricated top-gate flexible TTFTs using the a-IGZO film as an n-channel active layer on 200- μ m-thick polyethylene terephthalate (PET) films (Fig. 3a). Source, drain, gate contacts and a gate insulator were defined by standard photolithography and lift-off techniques. A ~140-nm-thick Y₂O₃ layer was chosen for the gate insulator and ITO (Sn:10%) was used for source, drain and gate transparent electrodes. These layers were deposited by pulsed laser



Figure 1 Schematic orbital drawings for the carrier transport paths (that is, conduction band bottoms) in crystalline and amorphous semiconductors. **a**, Covalent semiconductors have carrier transport paths composed of strongly directive sp^3 orbitals, so structural randomness greatly degrades the magnitude of bond overlap, that is, carrier mobility. Note that the orbitals shown are illustrative, and do not show exact wavefunctions.

b, Amorphous oxide semiconductors composed of post-transition-metal cations. Spheres denote metal *s* orbitals. The contribution of oxygen 2*p* orbitals is small. Direct overlap between neighbouring metal *s* orbitals is rather large, and is not significantly affected even in an amorphous structure.

letters to nature

deposition at room temperature using Y_2O_3 and ITO ceramic targets. The measured dielectric constant of the Y_2O_3 gate insulator was $\sim 16\epsilon_0$ (where ϵ_0 is the dielectric constant of vacuum), which is close to that reported for crystalline Y_2O_3 ($\sim 18\epsilon_0$)²⁵. The channel length and width were 50 µm and 200 µm, respectively (Fig. 3c).

The performances of the flexible TTFTs were measured in air at room temperature. Figure 4a shows typical source-to-drain current $(I_{\rm DS})$ -voltage $(V_{\rm DS})$ characteristics of a virgin device. The current $I_{\rm DS}$ markedly increases as $V_{\rm DS}$ increases at a positive gate bias $(V_{\rm GS})$, indicating that the channel is n-type. The $I_{\rm DS}$ reaches ~0.02 mA at a $V_{\rm GS}$ of 5 V. The $I_{\rm DS}$ - $V_{\rm DS}$ characteristics exhibit a clear pinch-off and current saturation, confirming that the TTFT operation follows the standard field-effect transistor theory. The saturation mobility $(\mu_{\rm sat})$ is obtained from the $I_{\rm DS}$ - $V_{\rm DS}$ curves in the saturation region using the equation $I_{\rm DS,sat} = (C_i \mu_{\rm sat} W/2L)(V_{\rm GS} - V_{\rm T})^2$, where C_i , $V_{\rm TD}$ W and L denote the gate capacitance, threshold gate voltage, channel width and length, respectively. The estimated $\mu_{\rm sat}$ value is ~8.3 cm² V⁻¹ s⁻¹, much larger than those obtained in organic and a-Si:H TFTs (the $\mu_{\rm sat}$ value ranges from ~6 to ~9 cm² V⁻¹ s⁻¹ in



Figure 2 Amorphous IGZO films. **a**, Glance angle X-ray diffraction pattern of the a-IGZO film deposited on a silica glass substrate at room temperature. No sharp peak is observed. CuK_{x1} radiation was used. Inset is the optical transmission spectrum of the film. The measured bandgap (E_g) is ~3.0 eV. **b**, Relationship between room-temperature Hall mobility and carrier concentration for a-IGZO films. Data on single-crystalline InGaO₃(ZnO)₅ films are shown for comparison. Electron mobility strongly depends on carrier concentration, and exceeds 10 cm²V⁻¹ s⁻¹ at carrier concentrations greater than 10¹⁸ cm⁻³, owing to potential distribution in the vicinity of the conduction band bottom (see ref. 23 for details).

the devices measured). Similarly, a field-effect mobility ($\mu_{\rm FE}$) estimated from the linear region in the $I_{\rm DS}-V_{\rm DS}$ curve (using $I_{\rm DS} = (C_{\rm i}\mu W/L)(V_{\rm GS} - V_{\rm T})V_{\rm DS})$ is ~5.6 cm² V⁻¹ s⁻¹ at $V_{\rm DS} = 2.4$ V, which agrees roughly with the $\mu_{\rm sat}$ value.

The transfer characteristic (Fig. 4b) shows that a low off-current, of the order of 10^{-7} A, and an on-to-off current ratio $\sim 10^3$ are obtained. The threshold gate voltage is positive ($V_T \approx +1.6$ V), showing that the TTFT operates in the enhancement mode (normally-off characteristics). The gate leak current is lower by several orders of magnitude than the source-to-drain current, which guarantees that the TFT characteristics are unaffected by the gate leak current. Small hystereses were observed in the $I_{DS}-V_{GS}$ curves with negative shifts in gate bias of 0.1–0.5 V at a scan speed of 0.5 V s⁻¹, which would be due to interface states.

Next, bending effects on the TTFT characteristics were examined.



Figure 3 Flexible TTFTs. **a**, Structure of TTFT fabricated on a plastic sheet. **b**, A photograph of the flexible TTFT sheet bent at R = 30 mm. The TTFT sheet is fully transparent in the visible light region. **c**, A photograph of the flexible TTFT sheet. The transparent TFT devices are made visible by adjusting the angle of the illumination.



Figure 4 Typical TTFT characteristics before and after bending. **a**, $I_{DS}-V_{DS}$ and **b**, $I_{DS}-V_{GS}$ characteristics before bending. The TTFT operates in the enhanced mode with a threshold voltage of ~+1.6 V. The saturation mobility is ~8.3 cm² V⁻¹ s⁻¹. On-to-off

The TTFT sheet was bent into a curve with a surface curvature radius (*R*) of 30 mm (corresponding to a tensile strain of ~0.3% in the TTFTs), as shown in Fig. 3b. The TTFT after bending maintained good characteristics, such as $\mu_{sat} \approx 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on-to-off current ratio of ~10³ (Fig. 4c, d). We stress that the TTFT performance is almost unaffected by bending, although a slight decrease is observed in the saturation current. After the initial bending, the TFT characteristics are stable and reproducible during and after repetitive bending. The TTFT is stable at temperatures up to 120 °C, but becomes inoperative at higher temperatures, probably owing to the softening of the PET substrate.

The present study demonstrates the room-temperature fabrication and operation of flexible TTFTs based on an amorphous oxide semiconductor, a-IGZO. TTFTs were fabricated on inexpensive polymer films and displayed good performance—such as saturation mobilities of ~6–9 cm² V⁻¹ s⁻¹, a low leak current of ~10⁻¹⁰ A, and an on-to-off ratio of ~10³—even during and after bending. We used pulsed laser deposition to form the active a-IGZO layer in this study, but a sputtering or metal-organic chemical vapour deposition (MOCVD) method can be used for large-area uniform deposition and mass production, as demonstrated for window electrodes of solar cells and flat-panel displays.

These achievements imply that transparent amorphous oxide semiconductors have the potential to overtake a-Si:H, and are promising materials for transparent flexible electronics. Furthermore, flexible TTFTs may be integrated with other alreadydeveloped devices that use a p-type amorphous oxide semiconduc-



current ratio is $\sim 10^3$. c, $I_{\rm DS}-V_{\rm DS}$ and d, $I_{\rm DS}-V_{\rm GS}$ characteristics after bending. The device was bent at R = 30 mm.

tor and p–n junction diodes fabricated at room temperature²⁶; this would extend the possibilities of flexible transparent electronic circuits. \Box

Received 4 July; accepted 5 October 2004; doi:10.1038/nature03090.

- 1. Huitema, H. E. A. et al. Plastic transistors in active-matrix displays. Nature 414, 599 (2001).
- 2. Kagan, C. R. & Andry, P. (eds) Thin Film Transistors (Marcel Dekker, New York, 2003).
- Yang, C.-S., Smith, L. L., Arthur, C. B. & Parsons, G. N. Stability of low-temperature amorphous silicon thin film transistors formed on glass and transparent plastic substrates. J. Vac. Sci. Technol. B 18, 683–689 (2000).
- Carey, P. G., Smith, P. M., Theiss, S. D. & Wickboldt, P. Polysilicon thin film transistors fabricated on low temperature plastic substrates. J. Vac. Sci. Technol. A 17, 1946–1949 (2000).
- Wang, S. C. et al. Device transfer technology by backside etching for poly-Si thin-film transistors on glass/plastic substrate. Jpn. J. Appl. Phys. 42, 1044–1046 (2003).
- 6. Shaw, J. M. & Seidler, P. F. Organic electronics: Introduction. IBM J. Res. Dev. 45, 3-9 (2001).
- Dimitrakopoulos, C. D. & Malenfant, P. R. L. Organic thin film transistors for large area electronics. Adv. Mater. 14, 99–117 (2002).
- Choi, H. Y., Kim, S. H. & Jang, J. Self-organized organic thin-film transistors on plastic. Adv. Mater. 16, 732–736 (2004).
- Lee, J. H. et al. Pentacene thin film transistors fabricated on plastic substrates. Synth. Metals 139, 445–451 (2003).
- Dimitrakopoulos, C. D. & Mascaro, D. J. Organic thin-film transistors: A review of recent advances. IBM J. Res. Dev. 45, 11–27 (2001).
- Taur, Y. & Ning, H. T. Fundamentals of Modern VLSI Devices (Cambridge Univ. Press, New York, 1988).
- 12. Kuo, Y. (ed.) Thin Film Transistors: Materials and Processes (Kluwer Academic, Dordrecht, 2004).
- 13. Thomas, G. Invisible circuits. Nature 389, 907-908 (1997).
- Kawazoe, H. et al. P-type electrical conduction in transparent thin films of CuAlO₂. Nature 389, 939–942 (1997).
- 15. Ohta, H. & Hosono, H. Transparent oxide electronics. Mater. Today 7, 42-51 (2004).
- 16. Wager, J. F. Transparent electronics. Science 300, 1245-1246 (2003)
- Hosono, H. Built-in nanostructures in transparent oxides for novel photonic and electronic functions materials. Int. J. Appl. Ceram. Technol 1, 106–118 (2004).
- 18. Madelung, O. (ed.) Technology and Application of Amorphous Silicon (Springer, Berlin, 2000).

letters to nature

- Hosono, H. et al. Working hypothesis to explore novel wide band gap electrically conducting amorphous oxides and examples. J. Non-Cryst. Solids 198–200, 165–169 (1996).
- Orita, M. et al. Amorphous transparent conductive oxide InGaO₃(ZnO)_m (m ≤ 4): a Zn 4s conductor. Phil. Mag. B 81, 501–515 (2001).
- Mott, N. F. Silicon dioxide and the chalcogenide semiconductors; similarities and differences. Adv. Phys. 26, 363–391 (1977).
- Narushima, S. *et al.* Electronic structure and transport properties in the transparent amorphous oxide semiconductor 2CdO/GeO₂. *Phys. Rev. B* 66, 35203 (2002).
- Nomura, K. et al. Carrier transport in transparent oxide semiconductor with intrinsic structural randomness probed using single-crystalline InGaO₃(ZnO)₅ films. *Appl. Phys. Lett.* 85, 1993–1995 (2004).
- Nomura, K. et al. Thin film transistor fabricated in single-crystalline transparent oxide semiconductor. Science 300, 1269–1272 (2003).
- 25. Kwo, J. *et al.* Properties of high *k* gate dielectrics Gd₂O₃ and Y₂O₃ for Si. *J. Appl. Phys.* **89**, 3920–3927 (2001).
- Narushima, S. et al. P-type amorphous oxide semiconductor, ZnRh₂O₄, and room temperature fabrication of amorphous oxide P-N hetero-junction diodes. Adv. Mater. 15, 1409–1413 (2003).

Competing interests statement The authors declare that they have no competing financial interests.

Correspondence and requests for materials should be addressed to H.H. (hosono@msl.titech.ac.jp).

Equilibrium cluster formation in concentrated protein solutions and colloids

Anna Stradner¹, Helen Sedgwick², Frédéric Cardinaux¹, Wilson C. K. Poon², Stefan U. Egelhaaf^{2,3} & Peter Schurtenberger¹

¹Department of Physics, University of Fribourg, Chemin du Musée 3, CH-1700 Fribourg, Switzerland

²School of Physics and COSMIC, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

³School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

Controlling interparticle interactions, aggregation and cluster formation is of central importance in a number of areas, ranging from cluster formation in various disease processes to protein crystallography and the production of photonic crystals. Recent developments in the description of the interaction of colloidal particles with short-range attractive potentials have led to interesting findings including metastable liquid-liquid phase separation and the formation of dynamically arrested states (such as the existence of attractive and repulsive glasses, and transient gels)1-7. The emerging glass paradigm has been successfully applied to complex soft-matter systems, such as colloidpolymer systems⁸ and concentrated protein solutions⁹. However, intriguing problems like the frequent occurrence of cluster phases remain¹⁰⁻¹³. Here we report small-angle scattering and confocal microscopy investigations of two model systems: protein solutions and colloid-polymer mixtures. We demonstrate that in both systems, a combination of short-range attraction and long-range repulsion results in the formation of small equilibrium clusters. We discuss the relevance of this finding for nucleation processes during protein crystallization, protein or DNA self-assembly and the previously observed formation of cluster and gel phases in colloidal suspensions^{12–17}.

A number of globular proteins have been shown to exhibit the major characteristics of colloids that interact via a short-range attractive potential. At high ionic strength, where the salt screens electrostatic repulsions, these short-range attractions increasingly dominate with decreasing temperature. This leads to a metastable liquid–liquid phase separation and related critical phenomena^{18–20}.

In agreement with predictions from mode-coupling theory⁹, there is also evidence for a glass or gel transition at low particle volume fractions and high interparticle attractions. Such a scenario obviously affects the ability to form the high quality crystals required for protein crystallography¹⁵. Using two apparently quite different model systems, we demonstrate the generality of this emerging description of the effect of a short-range attraction combined with either a hard or soft repulsion on the phase behaviour of a wide range of colloidal suspensions.

We first investigated solutions of the globular protein lysozyme (molecular mass 14.4 kDa, radius $R_{\rm m} \approx 1.7 \, {\rm nm})^{17-19}$. Using small-angle X-ray (SAXS) and neutron (SANS) scattering, we studied spatial correlations in concentrated solutions at low ionic strength, where the long-range repulsive electrostatic potential is only weakly screened. We then compared these findings with confocal microscopy results using colloid–polymer mixtures, a popular model system with easily tunable interactions. Here we used spherical colloidal particles interacting with a long-range repulsion resulting from a modest charge²¹ and a short-range attraction induced by a polymer-mediated 'depletion effect'²².

Figure 1 presents SAXS measurements on a lysozyme concentration series at 5 °C. The normalized scattering intensities I(q)/c, where I(q) is the scattering intensity at scattering vector q, and c is the protein concentration, show a forward intensity $I(q \rightarrow 0)/c$ that



Figure 1 Normalized scattered intensity I(q)/c and corresponding effective structure factors $S_{eff}(q)$, as obtained by SAXS from lysozyme solutions of different concentrations *c*. **a**, I(q)/c of a dilution series (3 mg ml⁻¹ to 273 mg ml⁻¹) at 5 °C. Large open circles represent the I(q)/c values extrapolated to $q = 0.1 \text{ nm}^{-1}$ and stars show the projection of the peak maximum onto the q-c plane. **b**, $S_{eff}(q)$ of the concentrated samples in **a**. Concentration ranges from 36 mg ml⁻¹ (open squares) to 273 mg ml⁻¹ (filled circles).