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Indications of bulk property changes from surface ion implantation

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In the majority of cases the effects of ion implantation are confined close to the implant zone, but potentially the resultant distortions and chemical modifications could catalyse relaxations extending into the bulk substrate. Such possibilities are rarely considered, but the present data suggest that high dose ion implantation of ZnO has induced bulk changes. Surface implants with Cu and Tb strongly modified the low temperature bulk thermoluminescence properties generated by X-ray irradiation. Suggestions are proposed, both for the possible mechanisms for bulk relaxations, and also structural characteristics which may imply where such instability could occur in other lattice structures.

Key words:- thermoluminescence, ZnO: Cu, ZnO: Tb, nanoparticles, phase transitions

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1 Introduction

Ion implantation is a highly successful and ubiquitous tool for the production of semiconductor components [1, 2]. Additionally there is an extensive literature in many fields for surface modification of other types of material. There are examples ranging widely from optical waveguide and photonic structures in insulators [3], to surface hardening and catalytic effects with metals [4, 5], to controlled production of nanoparticles [6]. In all such instances the primary objective has been to induce controllable and desirable changes in the surface of the host materials. Consequently the property changes that are measured focus on surface layers, and to a large extent the possibility that deeper features exist are mostly ignored. However, effects which extend a few microns beyond the implant have been noted, and these are mostly ascribed to the result of induced stress, or exciton and charge trapping. These effects are clearly important as any such distortions or changes of the original lattice will also occur laterally within the surface implant zone in patterned implant devices. By contrast, there has been negligible consideration, or experimental investigation, of the possibility of changes in bulk responses resulting from near surface ion implantation.

2 Potential materials that could demonstrate long range effects

Implantation in semiconductors requires small ion doses to achieve control of electrical conductivity, but with increasing ion implant concentrations several other effects develop. A primary factor is radiation damage, in which the structure is perturbed from the original crystalline or amorphous atomic arrangement, and this is

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3 accompanied by sputtering of atoms from the surface. Consequently the density of the
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5 layer is altered, and there are changes in composition both from preferential sputtering,
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7 and the injection of impurity ions. The chemical changes can result in new
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9 compounds, precipitates or inclusions [3, 6]. All these factors will allow local
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11 variations in the atomic packing density, the possibility for relaxations into alternative
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13 phases and an overall stress gradient relative to the interior of unimplanted material.
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15 Depending on the intensity of the stress gradient, implant temperature and subsequent
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17 annealing treatments, there is scope for further relaxation and inter-diffusion between
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19 ions in the implant and/or into the substrate regions. All such changes are familiar, but
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21 are either discussed as of minor importance, or considered as being limited to depths
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23 of, at most, a few microns beyond the implant zone. Hence damage, amorphisation or
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25 crystalline phase changes, of either the host or nanoparticle inclusions, are still
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27 considered as being relevant to a depth defined approximately by the primary ion
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29 range.
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36 With insulating materials there are further possible factors as ionisation can
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38 cause changes in valence and bond linkages [7-9]. Similarly, secondary electron
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40 ejection will cause locally intense electric fields across the insulating implanted layer.
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42 Each of these features will be sensitive to the original stoichiometry and initial degree
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44 of perfection in the host material. Potentially, the interface between the implanted and
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46 substrate regions can act as a nucleation plane from which relaxations and crystalline
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48 transformations can be initiated. Indeed, in annealing of amorphised silicon, the
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50 wavefront of crystalline regrowth moves rapidly from the interface through the
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3 amorphous implant. However, in many materials there is the potential for such
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5 seeding of relaxations and phase change to run from the implant zone into the bulk
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7 substrate. Obvious candidate materials for such long range lattice relaxations are
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9 crystals which intrinsically have a variety of metastable phases and/or are structurally
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11 sensitive to variations in stoichiometry, impurities or intrinsic defects. One assumes
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13 that bulk changes are most likely to be initially triggered in the highly stressed zone
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15 immediately adjacent to the implant region, and then this modified front propagates
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17 throughout the crystal. Equally, there may be relaxations driven by electric fields
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19 which develop during implantation of insulators.
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24 There are many materials that match these criteria for potential instability. For
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26 example in electro-optics and photonics a key material is lithium niobate [10]. It is of
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28 value precisely because the lattice is not totally stable, but can be easily deformed by
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30 pressure or electric fields. Consequently, it is extremely sensitive in terms of electro
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32 optic properties both as the result of dopants, and because it does not grow as a
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34 perfect stoichiometric material. Because of the commercial importance of LiNbO_3
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36 there has been nearly 50 years of intense effort associated with the crystal growth.
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38 Nevertheless, even “stoichiometric” LiNbO_3 still has lithium deficiency and a
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40 significant vacancy concentration, and the proton exchanged variants have a plethora
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42 of phase modifications as a function of temperature and hydrogen doping level.
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47 Lithium niobate is of further relevance here as one can reverse the direction of
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49 poling (i.e. the sequence of the ABCABC... structure formed by the Li, Nb and
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51 structural vacancy) either by heating and applying an electric field across the crystal,
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or by electron irradiation (which generates a space charge field).

For materials which have had less commercial investment in crystal growth, such as strontium titanate, silicon carbide, bismuth germanate or zinc oxide there are many conflicting reports of property differences, and even the presence of different crystal phases, which are all sensitive to supplier, impurities and growth conditions. Similar variations and sensitivity to the production are seen in coating layers that are deposited on a substrate (as used for optical applications). This process inevitably means they are non-stoichiometric, stressed, and with a high defect density. Further, thin film coatings are invariably structurally distorted at the interface with the substrate. Ion implantation into all such insulating materials could initiate structural relaxations. The implication is that, rather than being a rare event, the possibility of bulk relaxations induced by surface implants could be quite widespread. The dearth of relevant literature may be an indication of failure to seek such events, rather than a lack of examples.

3 Techniques to discriminate between surface and bulk property changes

For insulating materials extremely sensitive measurement techniques include luminescence and Raman studies since they respond to changes in lattice parameters and local defect environments. In order to record changes within an implanted surface region the luminescence excitation can be depth limited to separate the modified and bulk regions. Photoluminescence (PL) may be excited with band gap light so that the signals are generated in a near surface layer. Similarly, by varying the electron energy,

there is some control over the probe depth of cathodoluminescence (CL). Neither method is a perfect match to the ion implanted volume since both absorption of band gap photons, and electron energy deposition, are strongly depth dependent. Further, depending on ionisation, charge and exciton diffusion, the luminescence can originate at some distance way from the excitation site (typically much less than a micron). Even with such caveats it is simple to record spectral and lifetime changes of the luminescence within ion implanted surfaces of insulators. Data are then interpreted in terms of new localised defect sites, changes in lattice parameters, precipitates and inclusions.

To monitor the luminescence properties of the substrate, without contributions from the implant zone, is more difficult. In principle one may record PL and CL from the non-implanted surface of the crystal. Alternatively it is possible to record bulk luminescence signals during, or after, excitation with X-rays (RL –radioluminescence or X-ray induced thermoluminescence, (TL)). This is the approach used in the present work for very low penetration of surface implants (a few hundred nanometres) relative to the bulk material (millimetres). Since the implants only directly damage around ~0.01% of the material one assumes that the RL responses are still totally dominated by the bulk signals. Therefore if one records any significant changes in signal then these are related to bulk modifications caused by surface implants. Experimentally the luminescence signals are viewed from the non-implanted face to avoid any optical absorption within the implant layer.

Detection of such bulk changes from surface implants has been addressed for a

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range of insulating materials as part of a Sussex based programme to optically detect relaxations and phase changes. Of particular relevance is that data with SrTiO₃ clearly evidenced that surface implants could induce crystalline phase transitions throughout the bulk substrate [11-13].

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4 Experimental details

Nominally pure ZnO crystals were obtained from the Shanghai Institute of Optics and Fine Mechanic in China and the Juelich laboratory in Germany. Spectrally resolved thermoluminescence (TL) data were collected with a sensitive thermoluminescence system over the temperature range from 25 to 280 K. The details of this TL spectrometer have been reported before [14]. The signals are corrected for the wavelength dependent sensitivity of the detection system. One key feature of the data collection is that the spectra are taken with a wavelength multiplexed system, which cleanly identifies if different emission bands occur at different temperatures. A 6K/min heating rate was selected to minimize temperature gradients across the samples. Excitation for the TL was with X-rays and all samples were irradiated at 25 K and the radiation dose was 5 Gy.

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Samples were ion beam implanted with either Cu or Tb ions using a high ion beam current implanter in Juelich in Germany. The samples were implanted with 400keV ion energy with different doses (from 1.0x10¹⁶ to 2.5x10¹⁶ ions/cm² for Cu ions, and from 2x10¹⁶ to 2x10¹⁷ ions/cm² for Tb ions). One Cu sample implanted, with a dose of 1x10¹⁶ ions/cm², and a Tb sample with a dose of 2x10¹⁷ ions/cm² were

annealed in the air at 1,000°C for one hour. The post implant annealing was primarily intended to remove intrinsic implantation damage. However, within the implant layer such anneals are complicated as copper migration may well occur and, depending on the rate of cooling, copper nanoparticles may form within the layer.

As mentioned, to minimise distortion of the bulk TL signals in implanted samples the implanted face was on the heater block. This avoids absorption of light from the bulk of the crystal within the implant layer. This geometry implies that luminescence signals from the bulk material resulting from the X-ray irradiation should be observable under all circumstances.

The initial assumption would normally be that the bulk TL signal is unaffected by the surface implant and so this will be a constant signal in all samples (both original and implanted). New TL signals may well be generated by the ion implants and reconstruction of the implant ZnO layer and these will exist as additional features. Experimentally they may be difficult to detect relative to the bulk TL signals since the implant represents merely $\sim 10^{-4}$ of the volume of the total sample, particularly as for our samples there were relatively clear signals from the bulk region.

5 Results and comments

Initial material The initial TL measurements contrasted the differences and similarities of samples from the Chinese and German suppliers. An overall isometric view of the TL in terms of spectra and intensity during the TL heating are shown in figure 1. Figure 1a shows isometric data for a German ZnO sample. The contour map,

figure 1b, emphasises that the emission bands differ between the two temperature regions and also that at the higher temperature the “orange” and “red” signals peak at different temperatures. In broad terms there are strong emission features near 40K and a weaker set of signals near 160K. In detail there were minor differences in the low temperature spectra from ZnO from the two suppliers and a normalised comparison of their emission spectra is shown in figures 2. The wavelength sensitivity of the TL glow curves is indicated by figures 3a and 3b for material from the two suppliers, in which TL is compared between the Chinese and German material for the spectral bands of 550 to 650 nm (orange) and 700 to 750 nm (red).

These results indicate that, although there are minor differences in the emission spectra and TL from material between the two sources, the overall response pattern is similar in both cases. This suggests that the signals originate primarily from intrinsic type luminescence sites of the ZnO.

Effects of ion implantation Figure 4 offers examples of TL performance from ion implanted ZnO. Figure 4a is a TL plot of a sample implanted with Cu to a dose of 2.5×10^{16} ions/cm² and figure 4b shows the effect from using a dose of 2.0×10^{16} ions/cm² of Tb ions. Visually the two images are very similar but the more detailed TL plots for the two main emission band regions show some slight differences in terms of the relative heights of the bands. Figure 5a is for the Cu data and figure 5b is for the Tb implant.

Despite small differences between Cu and Tb samples it is clear that neither

isometric plot resembles that taken for unimplanted samples (as in figure 1a). In particular the low temperature signals have been completely suppressed, and the red signals seen near 140K have become very intense. The original red bands near 700 nm have been replaced with a feature at slightly longer wavelengths of ~730nm. On more careful inspection one notes that for the higher temperature peaks the orange and red features occur at different temperatures, with the 550 nm emission preceding the 730 nm glow peak by ~15 degrees.

Post implant annealing One sample, which had received a smaller ion dose of 1×10^{16} ions/cm² of copper was annealed at 1,000°C to test if the changes in TL response were sustained after annealing. The isometric data are shown in figure 6 and spectrally resolved TL plots are presented in figure 7a and 7b are for orange and red emission. Signals for the original unimplanted ZnO are included for comparison.

Whilst there are now signals at the lower temperatures after the annealing treatment, the form of the glow curves and the position of the emission bands are significantly different from the original data. Annealing has added new complexity to the signals, rather than just regenerating the pre-implant data. Annealing has however retained a strong red emission peak, even though it has moved in TL temperature.

6 Discussion

The objective of this experiment was to consider if high dose surface implants, with penetration depths of a few hundred nanometres, have any detectable influence

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on the bulk luminescence signals of ZnO crystals. The advantages of the x-ray excited low temperature TL is that the measurement does not introduce any thermal heating after the implantation and, since the implant volume is only $\sim 10^{-4}$ of the sample volume, the bulk signals should be retained. New TL features from within the implant volume may exist, but such signals may be overshadowed by the bulk signals. The reality is that the surface implants have totally modified the bulk signals, as is seen by comparing figures 1 and 4. This is extremely clear evidence that the bulk ZnO is showing different TL response to the X-ray excitation.

Whilst these data satisfy our original objective of demonstrating very long range effects in an insulator as the result of surface implants, the results do not reveal the mechanism for the change, nor the precise changes which have occurred. The discussion of the mechanisms and modifications which occur must therefore be very speculative. Nevertheless, the detection of such changes has significant implications for consideration of ion implantation in many types of material.

This is not the first demonstration of such effects as we have conducted quite detailed studies of luminescence signals from strontium titanate [10-13]. The SrTiO₃ case was perhaps less surprising as it is known to be structurally very sensitive to impurities and growth conditions, and the relevant literature has many anomalies and conflicts as to how many low temperature phase transition, or relaxations, can occur. Therefore the interpretation for SrTiO₃ was that stress generated from the implant layer was sufficient to induce phase changes. Further, there were discontinuities in the temperature dependence of the luminescence signals, which are characteristic

signatures of phase transitions, and indeed they occurred at temperatures which matched critical points discussed in the strontium titanate literature.

For ZnO it is less obvious if there have been any phase changes as there are no discontinuities in the luminescence signals with temperature. This does not exclude the possibility that the lattice parameter has not been modified, or that stress or electric field derived from the implant zone have not introduced asymmetry into the lattice structure. Volume and distortion changes in the lattice will of course modify the intrinsic (and impurity) luminescence sites and will shift the glow peak temperatures. Such TL peak shifts as a function of lattice distortion have already been reported in several other insulating materials.

ZnO was chosen for this experiment as it is unlikely to be fully stoichiometric [15] and it is known from the higher temperature studies that it can relax under high pressure and even undergo phase transitions, deform readily and is sensitive to impurities [16-18]. The normal material is a hexagonal (wurtzite) structure but cubic variants have been formed. For non-stoichiometric or impure material, lattice perfection is suspect. Interestingly, it has been claimed that ZnO can form the richest family of nanostructures [19]. The excellent non-linear and piezo- or electro-optic properties also imply structure with the potential to readily distort. Similarly the measurement of photoluminescence or cathodoluminescence has generated a literature where the emission spectra are extremely varied both in terms of peak position, substructure, and different relative intensities of the nominal green and red emission bands. Variations are invariably a key indicator that the materials are non-

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stoichiometric, distorted or contain a variety of defect clusters and/or impurities. Such situations therefore have the potential for the crystal to distort and relax into alternative stable zones under stress or electric fields.

In terms of luminescence efficiency and the types of defect which contribute to the TL signals it is essential to note that the older models of highly localized defects are inappropriate (e.g. as reviewed in [20]). Instead one must recognize that luminescence efficiency is strongly influenced by many neighbouring shells of lattice ions. The more sensitive experiments and calculations suggest that “point” defects can influence many thousands of neighbouring ion sites. Thus distortions of the local symmetry, for example by a uniaxial stress induced from the implant surface, relaxations of the basic lattice spacing, or even, in an extreme case conversion to a new crystalline phase, would all change the emission site properties. This would be reflected by changes in emission spectra and shifts in the glow peak temperatures, as seen here for ZnO. The parallel experiments with SrTiO₃ identified that, at least in that lattice, the ion implantation stress can induce phase transitions. Equally clear is that in many materials long range effects exist from phase changes of nanoparticle inclusions. In each situation there are changes in luminescence efficiency and emission spectra. The use of luminescence to detect such phase transitions and relaxations has recently been reviewed [21, 22].

The temperatures at which glow peaks occur are similar to the critical temperatures at which ESR defects anneal or convert into different species. In particular the lowest temperature signals match to charge release of holes as

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interstitial diffuse [23-27]. Signals in the region of 150 K have been linked to annealing of oxygen vacancy (V_O) centres. All three charge states of V_O , V_O^+ , V_O^{2+} have been reported, and the V_O^+ decays into a V_O with an activation energy of $\sim 0.3\text{eV}$, [27, 28] corresponding to TL activation energy of the 150K type features.

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In terms of spectra the emission bands noted during the TL measurements are broadly consistent with luminescence bands discussed elsewhere for ZnO and which are generally ascribed to intrinsic defects. Nevertheless the literature, although extensive (e.g. [15, 19, 23-37]) is not totally satisfactory, as a large fraction of the studies which mention luminescence relate to thin film or particulate size ZnO, or material which is doped. The films and small particle work is thus biased by problems of non-stoichiometry and the importance of surfaces and grain boundaries. Both green and yellow emission bands are cited with varying models based on intrinsic, or intrinsic plus impurity, sites. The features seen here near 590 nm might fit to the "yellow" emission bands but there are obviously a number of component features.

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There have been studies of copper doping in ZnO [29], which activates green emission near 510 nm. For our copper implanted samples recorded there is no obvious enhancement of emission in that range. Indeed since the copper would be confined to the tiny implant surface zone any such X-ray stimulated TL signals would be very small compared with those from the bulk material. One also notes that the spectra from Cu and Tb implants were very similar, so it is lattice damage that is important for this data.

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7 Conclusion

The experimental data strongly indicate that ion implantation with Cu or Tb into ZnO can result in changes in the luminescence responses of the bulk material. Mechanisms for the bulk changes are speculatively linked to stress or electric fields generated by the surface implants which modify the bulk structure.

This is not the first example of such an effect and it may be indicative that many other non-stoichiometric or metastable crystalline structures undergo similar long range relaxations and/or phase changes as the result of surface treatments. The dearth of a relevant literature probably reflects a lack of investigations, rather than a rarity of such effects. Whilst luminescence measurements do not offer models of the defect sites they do at least reveal a number of participating defects and also clearly demonstrate the more subtle changes from the original lattice.

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Figure captions

Figure 1 Low temperature thermoluminescence from ZnO after X-ray irradiation at 25 K for a heating rate of 6 K/minute. (a) an isometric view and (b) a contour map which emphasizes that different spectral regions peak in intensity at different temperatures.

Figure 2 Comparisons of 40 K TL emission spectra from samples from different suppliers.

Figure 3 Wavelength resolved ZnO TL curves for the orange and red emission regions. (3a) is for a Chinese sample and (3b) for one from Germany.

Figure 4 The isometric view of the TL emission after the surface had been implanted with high doses of (a) Cu and (b) Tb ions.

Figure 5 Examples of wavelength resolved TL for implanted samples, (a) after Cu implantation and (b) after Tb implants.

Figure 6 The glow curve of a copper implanted annealed ZnO sample.

Figure 7 Spectrally resolved TL for (a) orange and (b) red emission of ZnO for three stages of treatment. The plots include TL of an original crystal, data for a Cu implanted sample, and the TL patterns seen after a Cu implanted sample had been annealed.

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Indications of bulk property changes from surface ion implantation

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Figures

Figures and captions

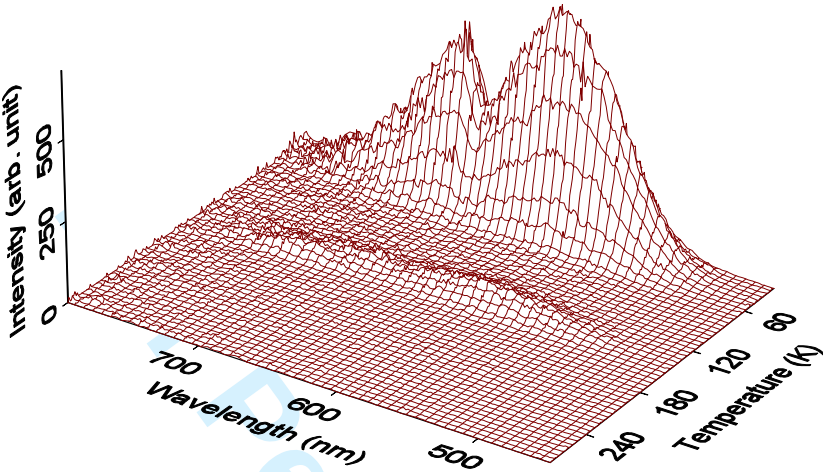


Fig 1a

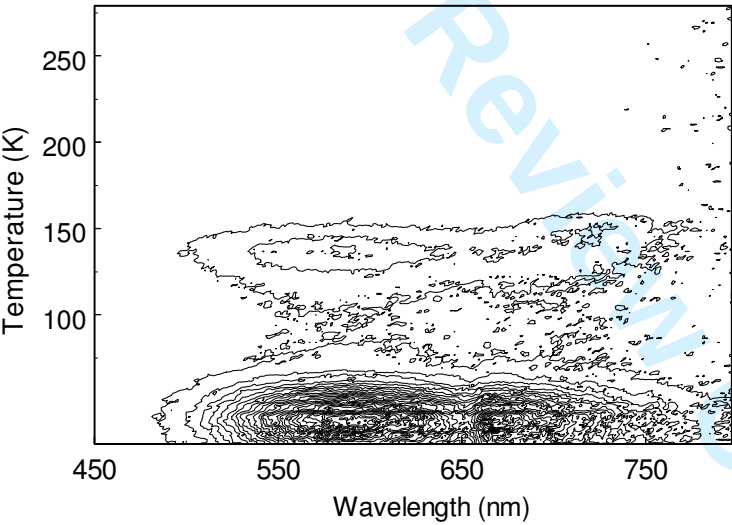


Fig 1b

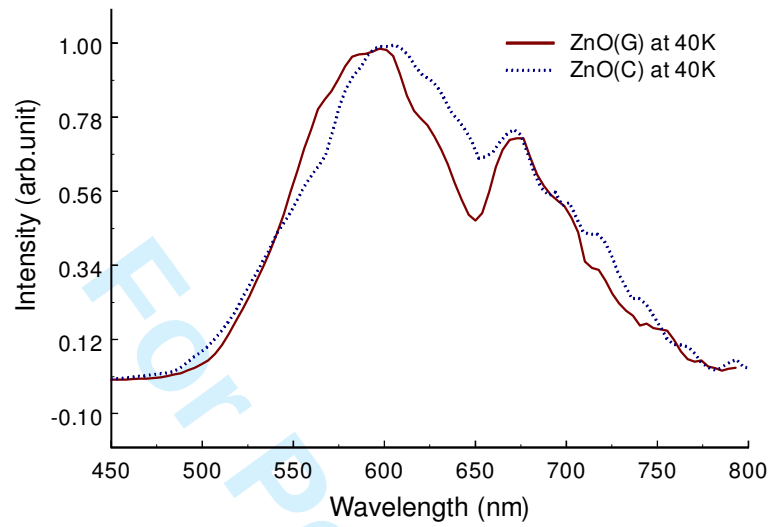


Figure 2

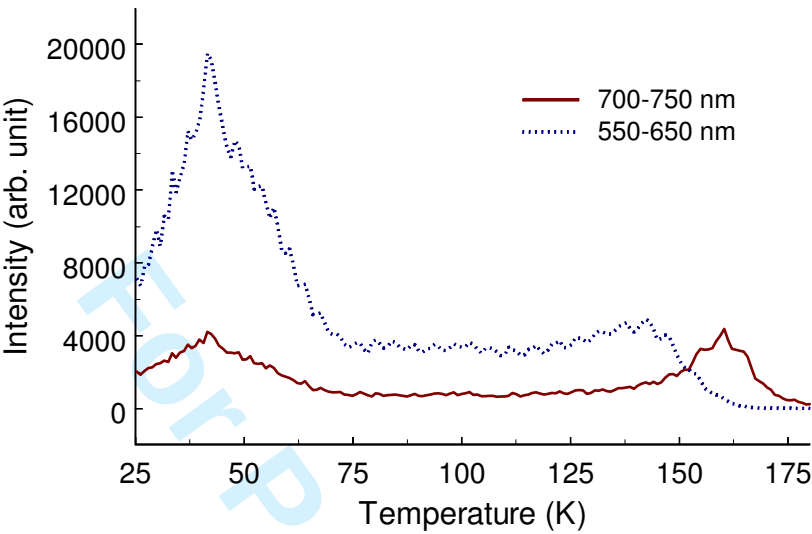


Fig 3a

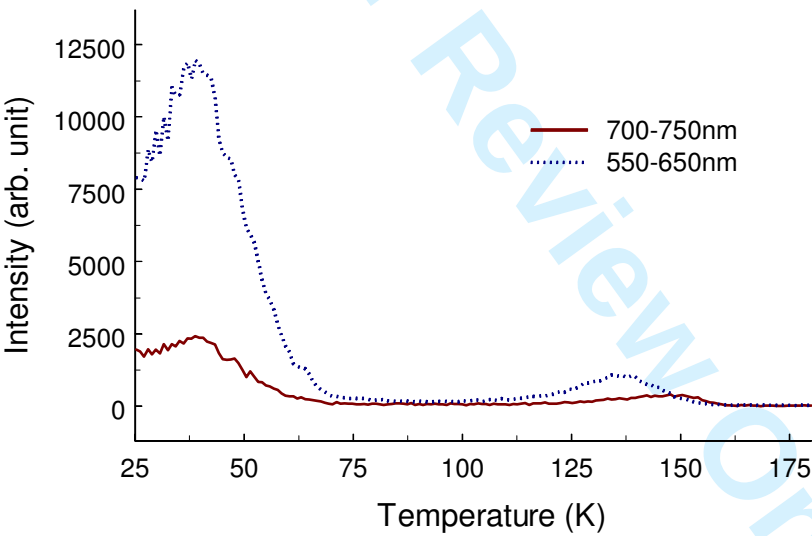


Fig 3b

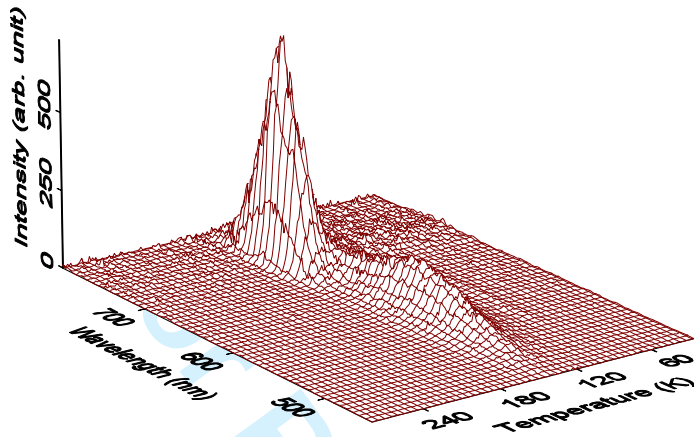


Fig 4a

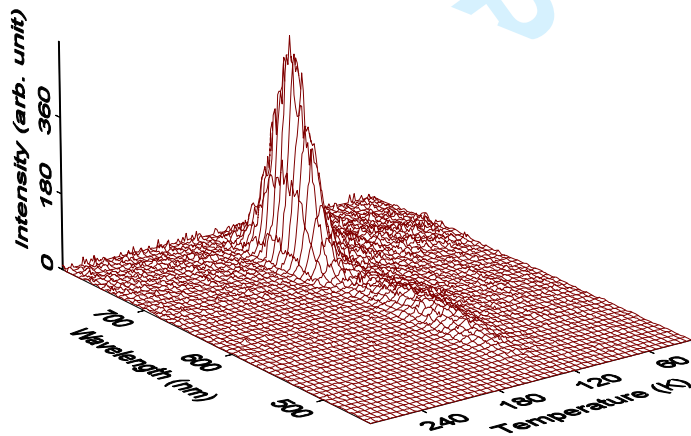


Fig 4b

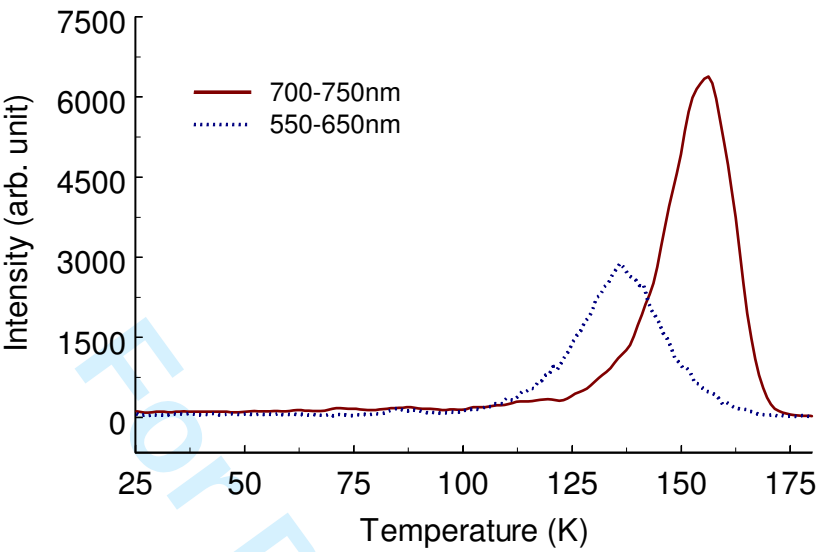


Fig 5a

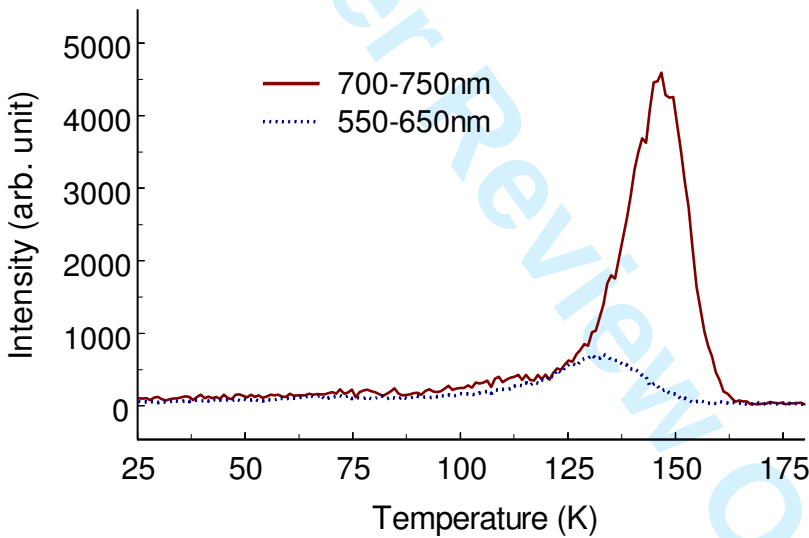


Fig 5b

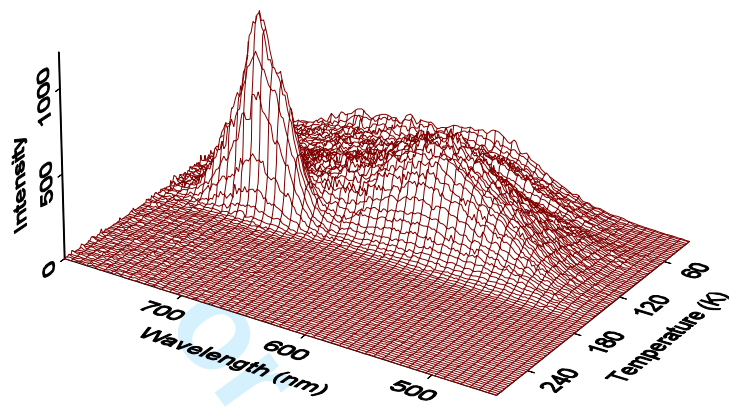


Figure 6

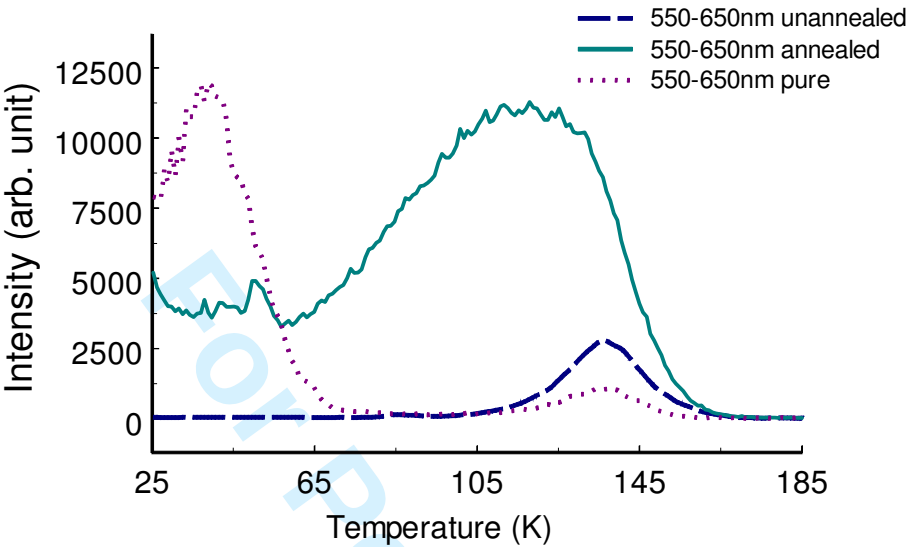


Fig 7a

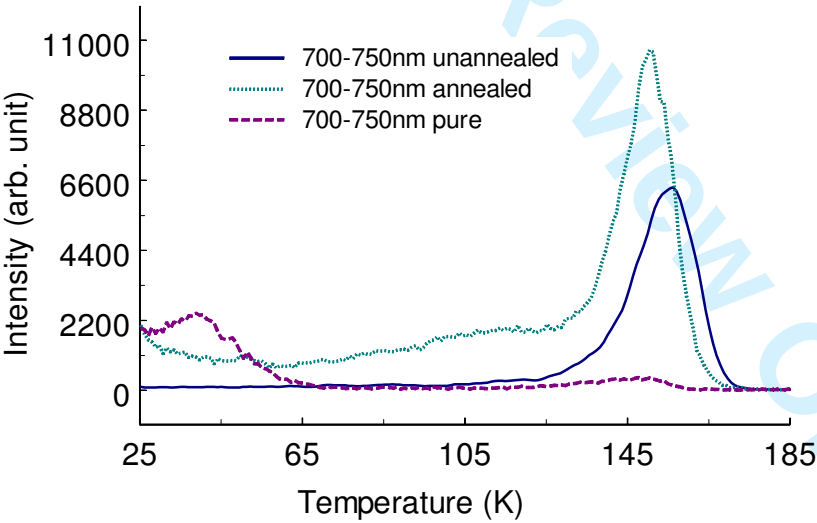


Fig 7b