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**Pulsed Laser Deposition of thin films for lasers and quasi-phase matched devices**

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**14. ABSTRACT**  
 The work performed under this award focused on the growth by Pulsed Laser Deposition, at the University of Southampton, of thin films of Ti-doped sapphire, intended for lasing waveguide applications, and their subsequent characterization at AFRL in terms of surface profilometry and Ti concentration. A range of films was analyzed, principally by SIMS, to evaluate Ti concentration, and to attempt to correlate the results with: 1) alternative measurements such as EDX, XPS and PIXE obtained by other labs, and 2) the PLD growth parameters used. One of the major (and on-going) problems is the precision with which dopants such as Ti can be measured when concentrations are in the sub 0.1% level. Techniques that are readily available, such as EDX (energy dispersive x-ray analysis), have problems with accuracy, and can have detection limits that are far from equate for this problem. There is the additional problem that lines can as shown below (spectrum recorded at Southampton), which further limits the possibility of quantitative determination.  
 This was the basis for the work that was undertaken between Southampton and AFRL, namely the quantitative assessment of Ti dopant concentrations in a range of PLD grown samples. Complications, to be further discussed below, for such low concentrations also revolve around: 1) matrix considerations (the underlying quality of the sapphire host), 2) the unknown concentration of Ti in the original PLD target. 3) availability of a comparison sample with known Ti concentration for normalization of SIMS analysis.

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## End of award report from University of Southampton.

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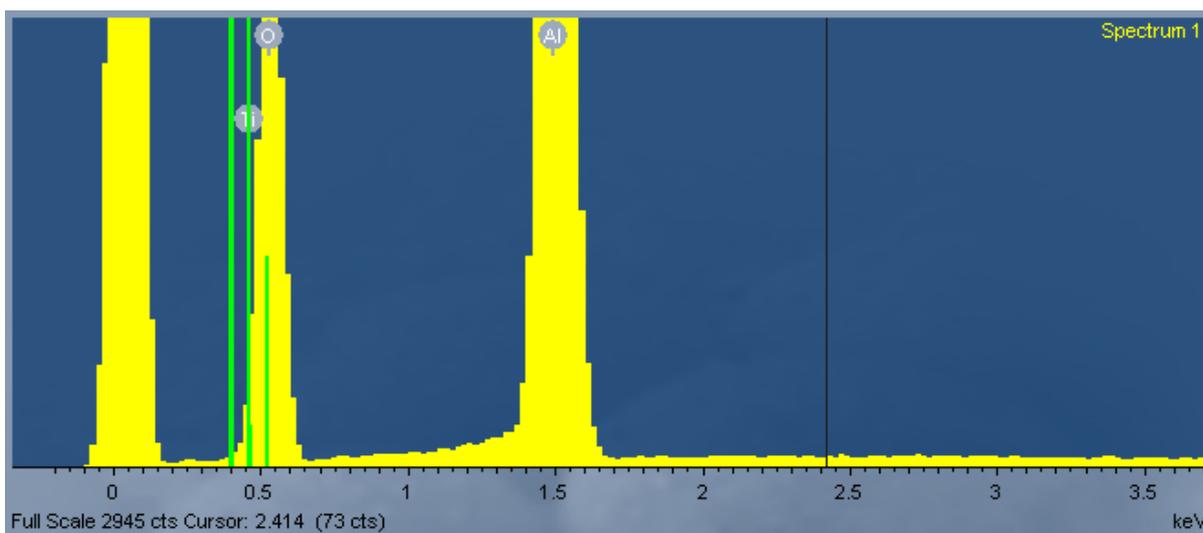
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### Background to the work:

The work performed under this award focused on the growth by Pulsed Laser Deposition, at the University of Southampton, of thin films of Ti-doped sapphire, intended for lasing waveguide applications, and their subsequent characterization at AFRL in terms of surface profilometry and Ti concentration. A range of films was analyzed, principally by SIMS, to evaluate Ti concentration, and to attempt to correlate the results with:

- alternative measurements such as EDX, XPS and PIXE obtained by other labs
- the PLD growth parameters used.

One of the major (and on-going) problems is the precision with which dopants such as Ti can be measured when concentrations are in the sub 0.1% level. Techniques that are readily available, such as EDX (energy dispersive x-ray analysis), have problems with accuracy, and can have detection limits that are far from equate for this problem. There is the additional problem that lines can as shown below (spectrum recorded at Southampton), which further limits the possibility of quantitative determination.



**Figure 1. EDX spectrum of Ti: doped sapphire thin film.**

From figure 1, it is clear that the overlap problem is acute for the titanium line (second green vertical bar) and oxygen (third green bar), so that any kind of accurate estimation is impossible, given that the ratio of oxygen to titanium concentrations may be in excess of 1000.

However, EDX is both fast and routine, so there is a natural tendency to be influenced by such a measurement, even though it is known *a priori* that the results will be qualitative at best. The further appeal of EDX is that it is non-destructive, and can be performed at the same time as scanning electron microscopy. Experimenters who have used EDX to measure elemental concentrations at the level of ~1% and above (the normally accepted minimum

value for EDX) will naturally assume that their measured value of 0.05% (for example) for Ti in Ti: doped sapphire 'means' something. Unfortunately, in quantitative and publishable terms, it doesn't, and hence when a competing technique such as SIMS or XPS is used, both of which are far less routine, much more costly in terms of time and preparation, and which may also be destructive to the film itself (in the case of SIMS), and finally generate a very different result to EDX, there is the feeling that the lack of expected agreement is somehow systematic of the measurement process itself, and the quantitative assessment of such low concentrations will prove ultimately elusive.

This was the basis for the work that was undertaken between Southampton and AFRL, namely the quantitative assessment of Ti dopant concentrations in a range of PLD grown samples. Complications, to be further discussed below, for such low concentrations also revolve around:

- matrix considerations (the underlying quality of the sapphire host)
- the unknown concentration of Ti in the original PLD target
- availability of a comparison sample with known Ti concentration for normalisation of SIMS analysis.

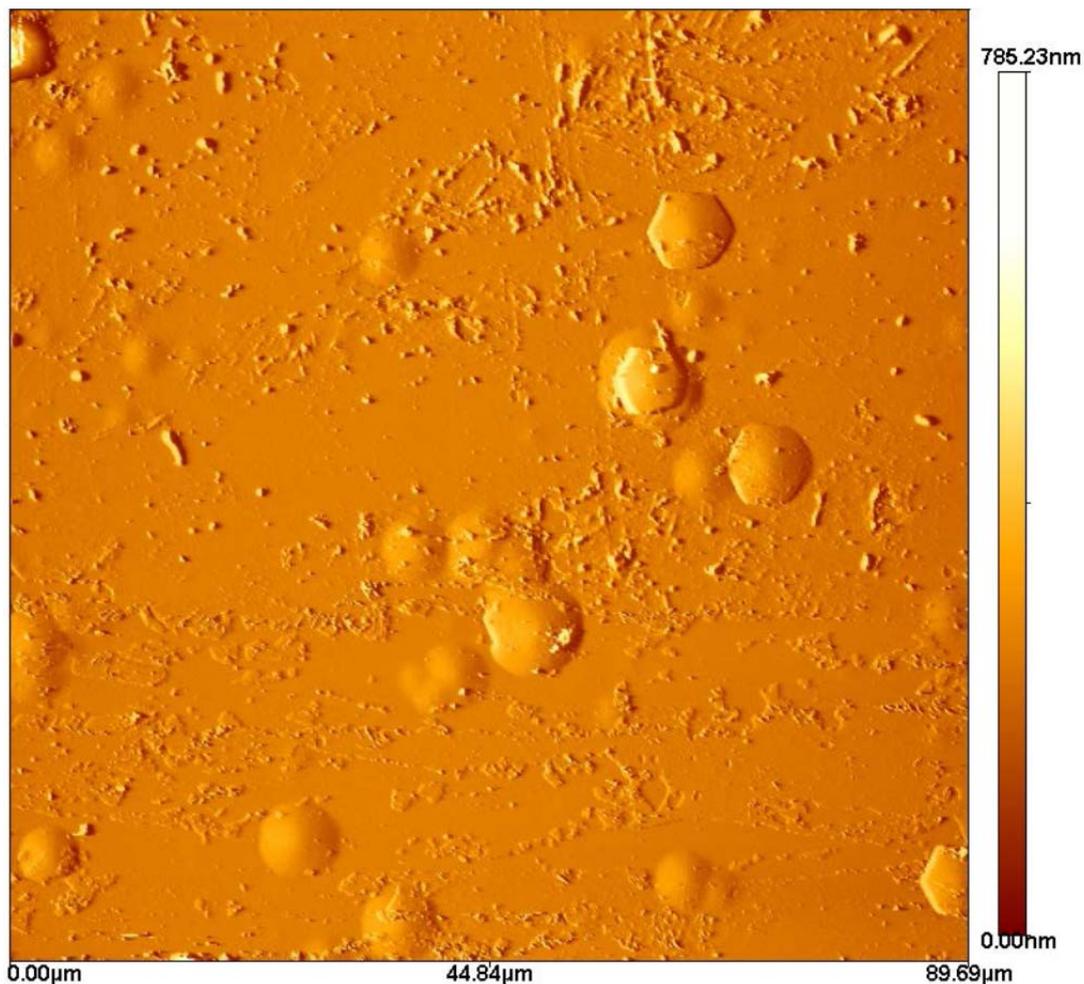
We will take these 3 points in order and discuss the progress made for each during the course of the award.

### **1. Matrix considerations.**

In common with many analysis techniques, the host matrix is an important consideration particularly when quantitative determination is required of elemental compositions that fall below the  $\ll 1\%$  level. Techniques that involve charged particles (electrons, ions) for either excitation of the impurity or dopant to be analyzed (for example EDX and PIXE), or collection of secondary ions (SIMS) are always complicated if the sample under analysis is an insulator: build-up of charge on the sample surface will distort the final result, and in some cases the signal measured will erroneously vary with time. Naturally, this adds myriad complications, as the signal obtained will be a convolution of sample charging artifacts and possible actual dopant variation with depth.

In addition, it is important to know in advance the topography of the sample surface as impurity inclusion can in principle be different in features that are growing proud of the underlying surface.

Figure 2 shows an example atomic force microscope (AFM) picture obtained at AFRL, which does show such raised surface features. In this case the hexagonal-shaped features are important, as they prove that the growing film possesses the underlying hexagonal crystal structure of sapphire, and that all of these hexagonal shapes are oriented in the same direction, indicating oriented epitaxial growth.



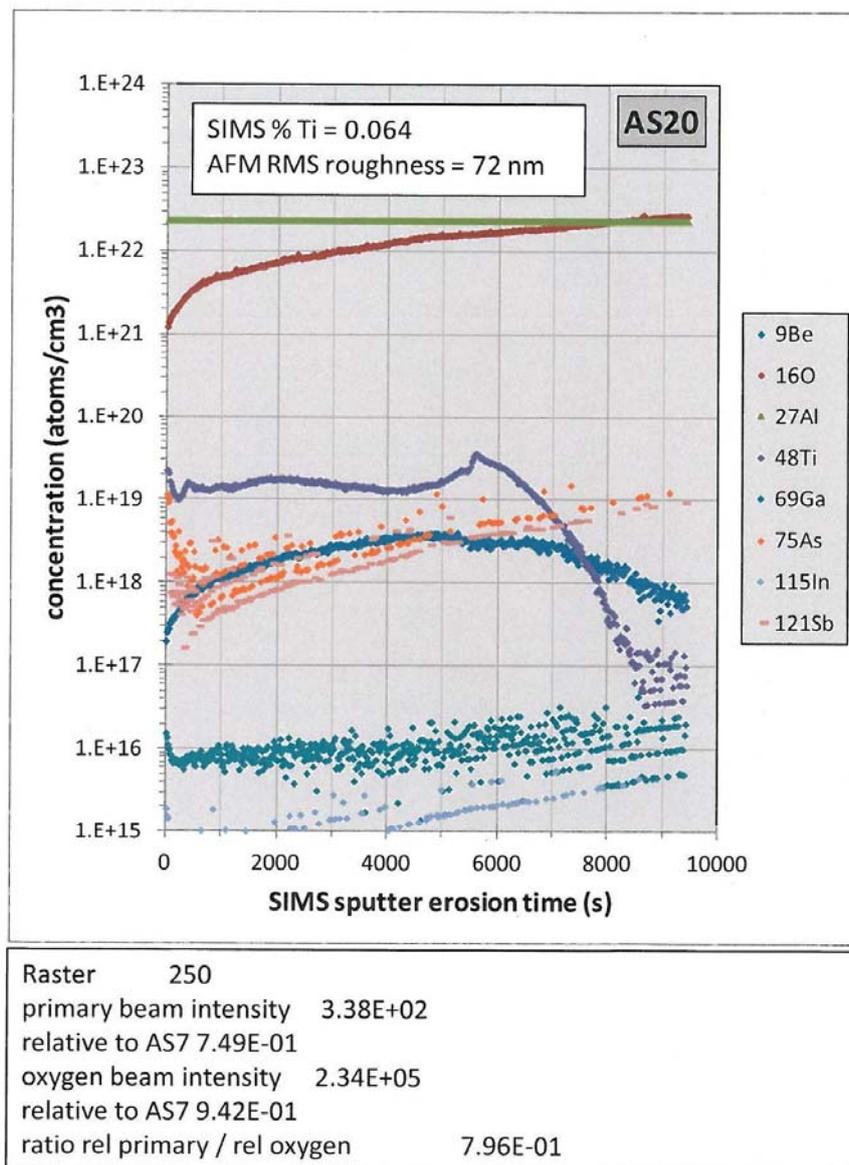
**Figure 2. AFM image of surface of PLD grown Ti: sapphire thin film**

What is more important however is to develop a SIMS procedure for forcing such highly non-conductive samples to surrender their secondary ions to the detector in the SIMS instrument. If this is not done, then all results are under question, both in terms of absolute quantification as well as their time-dependency.

As a further example of what is meant by time-dependency, we show in figure 3 a SIMS result for a particular sample, that raises several important points and questions. In order of importance these are:

- measured concentrations are seen to be a function of depth within the sample.
- the measured (SIMS) concentration for oxygen and aluminium within the host crystal (sapphire =  $\text{Al}_2\text{O}_3$ ) are clearly wrong. The apparent variation of the oxygen signal with depth is likely due to element-specific, depth-dependent charging, and shows the necessity of eliminating the sample charging instead of *a posteriori* correction of the SIMS data. For early times (shallow depths) the relative ratio measured for Al:O is of order 10:1. This is clearly an error, as the atomic ratio is 2:3, and hence there is an implied and fundamental error of x 15 in the data presented.

- The Ti concentration is approximately correct at  $\sim 0.1\%$  compared to the (fixed) value of Al, but this same concentration is also apparently present for As, which to the best of our knowledge is not present (or should not be present) within the Ti: sapphire films.



**Figure 3. SIMS data for sample AS20 obtained at AFRL**

All three of these factors are of concern for quantitative assessment of such low concentrations of dopant. The way forward that has been identified is to use a calibration sample (see later for details) that will act as a comparator. A sample has been bought via AFRL, and we await further SIMS results that should prove to be more quantitative.

On a more positive note, figure 4 shows another SIMS result in which the Ti concentration is seen to fall dramatically at a time of >2000s. The Ti concentration appears to be relatively flat, and again is at the ~0.1% level compared to Al.

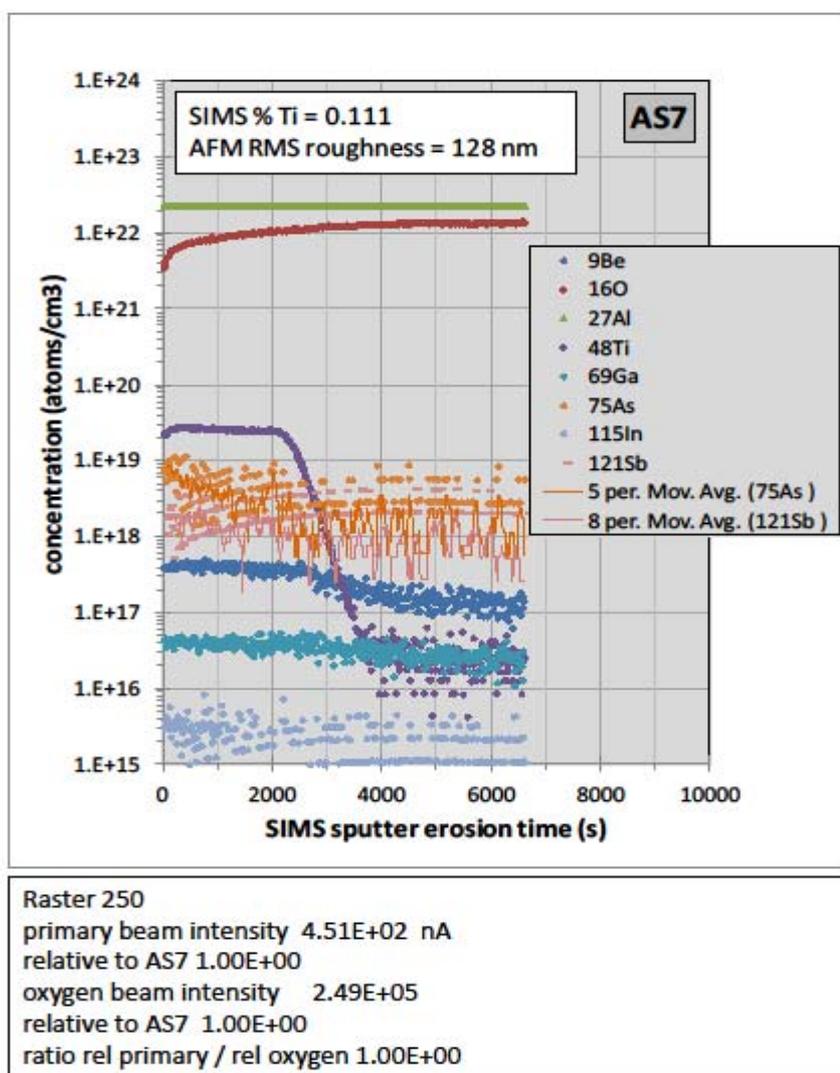


Figure 4. SIMS data for a different sample (AS7) which shows clear fall in Ti: concentration

## 2. Concentration of Ti in PLD target

A useful method of calibration (for both EDX and SIMS) is to use a standard which has a known concentration of the element or impurity under investigation, and to cross-calibrate the experimentally measured result with the concentration that is specified in the standard.

This can work well provided that:

- The standard has a known concentration of the desired element, and that it has been measured reliably.
- The standard can be used for quantitative subsequent analysis via SIMS (or EDX or other techniques)

This technique suffers however from two major considerations.

Firstly, the supplier of our original Ti:sapphire single crystal target was unable to specify the Ti concentration to better than the values of 0.1-0.2 at%. We tried to measure the actual value, but fell into the same problems as we encountered as measuring Ti concentrations in the PLD grown films.

Secondly, during PLD, although the technique is advertised as being capable of maintaining the stoichiometry present in the target, this is not always true. Loss of a particular element can be severe, and for some elements in particular (fluorine, sulfur, chlorine, lithium..) elemental loss can be high, in some cases approaching 50% and more. Knowing the concentration in the target, while desirable, does not therefore translate into a direct knowledge of concentration in the films grown.

This chicken-and-egg situation is far from satisfactory, and was the basis under which we had welcomed SIMS analysis.

### **3. Use of a known standard**

We are now fortunate in having a calibration standard, purchased by AFRL, for use in subsequent analysis, and have also started using a PLD target that has a higher (specified at 0.2-0.4 at%) concentration of Ti, and have grown a series of new films. We will be sending some of these new films for SIMS calibration, and hope to further establish the concentration of Ti and perform more quantitative measurements.

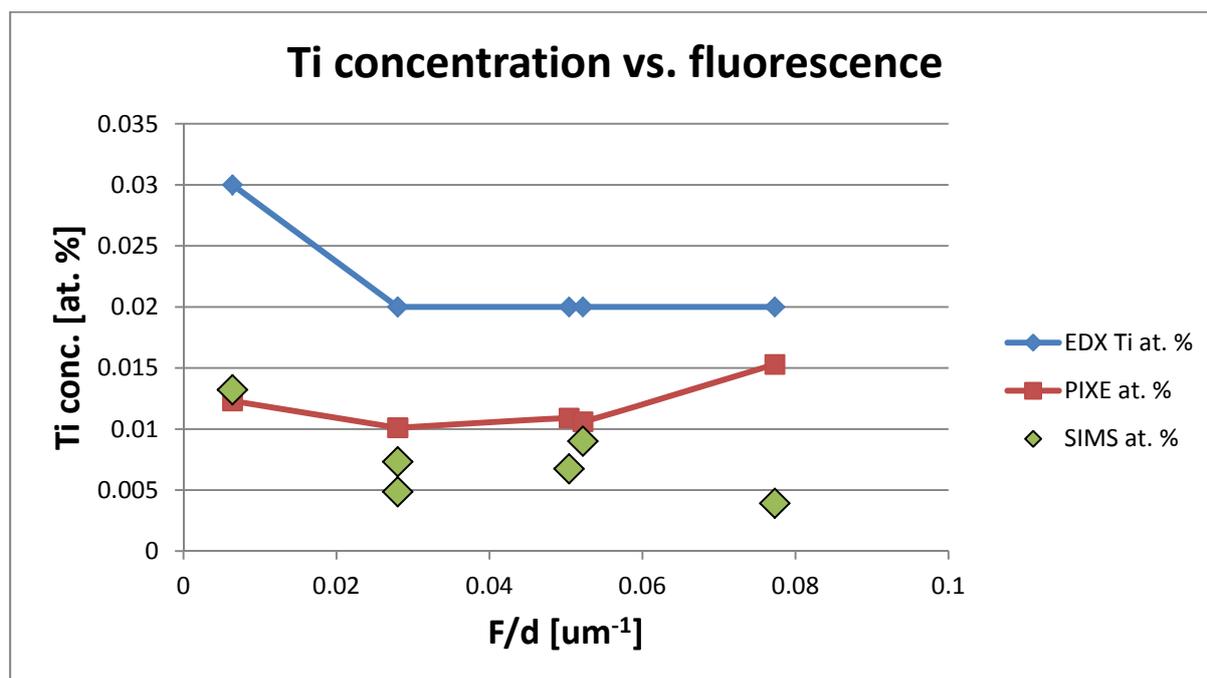
Ti concentration is important for a range of reasons, not only for the gain and lasing properties of the waveguides, but also because it is the presence of Ti in the sapphire lattice that leads to the required refractive index change that produces waveguiding in the first place. Knowledge of Ti concentration is therefore important as it determines all of:

- The required waveguide thickness for single mode guidance.
- The gain per unit length of the waveguide structure.
- The length of the guide for effective absorption of the pump light: too short, and pump light is inefficiently absorbed; too long and the guide contributes more to passive loss rather.

The use of this standard and suitable cross-correlation should finally yield quantitative results for Ti concentration.

## Results to date.

Within the experimental uncertainties described earlier, figure 5 shows a composite measurement of Ti concentrations in a range of films measured so far. As noted earlier, the EDX data is practically of little use, and should not be used for anything quantitative. The PIXE data, obtained at the University of Surrey, UK, shows a limited agreement with the SIMS data, but there are some distinct discrepancies, (for example the results for F/d of  $\sim 0.075$ ).



**Figure 5. Summary of measurements of Ti concentration by EDX (Southampton), PIXE (University of Surrey, UK) and SIMS (AFRL).**

What is interesting, and also currently unexplained however is the following:

For each film, a quantitative assessment was made of the fluorescence output at a wavelength of  $\sim 800\text{nm}$ , and a value normalized to the film thickness was then evaluated, which appears in figure 5 as Fluorescence / film thickness, or F/d. What is expected is that the most fluorescent film would have the highest concentration of Ti, but from both PIXE data and more especially the SIMS data, an inverse correlation would appear to hold. It is unexpected for example that the most fluorescent film would feature the lowest Ti concentration.

More work needs to be done on this aspect, and when the calibration standard is used, this anti-correlation may be explained.

**Additional benefits from the AFRL collaboration**

Aside from the measurements being undertaken, there is a separate benefit from contact and discussions between Southampton and AFRL, concerning PLD research in general. The offer has been made for a current student to visit AFRL, and interact over multibeam PLD technique, and, time-willing, this would clearly benefit both parties.

In fact both sides would welcome a continuation of this award and the principal investigator at Southampton also has plans for a visit to AFRL in 2013. If there is the possibility to extend or renew, then this would be very valuable.

This work allows AFRL to expand its SIMS characterization expertise to have reliable, quantitative SIMS capability for measuring impurities in very thick, highly non-conductive films. This will be valuable for other materials of importance to AFRL, such as characterization doping and impurities in wide-band gap semiconductors, and for characterizing the composition of high-dielectric constant capacitor materials.

Professor Robert Eason

09/10/12