The successful production, via two different oxidation processes, of metal-oxide-metal (MOM) diodes is presented. An innovative reactive ion etching and plasma assisted regrowth process has been used to provide oxides, which are in the thickness range 4.0–5.1 nm. These are thinner and physically more uniform than oxides grown in a furnace, resulting in diodes which should conduct via electron tunnelling across the MOM junction. Transmission electron microscopy analysis has been used in conjunction with time of flight secondary ion mass spectrometry analysis to verify oxide thickness and uniformity.

1. Introduction: Metal-oxide-metal (MOM) diodes have the potential to rectify terahertz radiation collected by micromachined antennas from waste heat sources and thus convert this into a useful DC current. This antenna-coupled diode structure can be used to detect and recover infrared radiation, thus acting as a useful energy recovery device. Other researchers produce these structures to detect CO$_2$ lasers, which operate near 30 THz, for example [1], thus confirming their ability to function at such high frequencies.

The antennas themselves are produced using standard lithographic techniques, with micronscale dimensions; however, the diodes must be much smaller than this, their production and characterisation being the focus of this research.

The MOM diode structure consists of two dissimilar metals separated by a native oxide layer, which is sufficiently thin to allow electron tunnelling to occur, that is, up to 5 nm thick. A functional MOM diode can be achieved by using one metal which will oxidise readily and another which is inert, with a native oxide being grown in between the two. Maximising the work function difference [2] between these metals is also beneficial as it increases the asymmetry of the resulting diode. A number of metal combinations have been used [1, 3]: here, we have chosen titanium, which oxidises readily, and maximised the work function difference by using inert platinum as the second metal.

As discussed, the oxide layer which separates the metals must be sufficiently thin to allow electron tunnelling to occur, as electron tunnelling is considered to be the conduction mechanism of choice for such devices because of its inherent speed (here the diodes are only limited in speed by the RC constant of the rectenna configuration [4]). Initial production of diodes using furnace oxidation of the titanium layer resulted in oxides which were in the region of 6–7 nm thick, which is not sufficiently thin for tunnelling [5]. This presents a major research challenge; a material must oxidise readily, but the oxide must equally be of a controlled, and very small, thickness. To achieve a balance between these two competing demands would suggest the need for a means of removing a metal oxide in its entirety, and then instantaneously regrowing an oxide in a controlled and reproducible way. This would further suggest that the two processes would need to occur sequentially in a vacuum, that is, in practice in the same processing tool. This Letter concentrates on achieving this using a combined reactive ion etch/plasma etch (RIE/PE) tool, where RIE is first used as the oxide removal technique, and a low power PE mode in an oxygen environment is then employed to regrow the oxide to a required, controlled thickness.

2. Fabrication: The fabrication process is shown in Fig. 1. Initial process testing took place on N-type (100) silicon of 10–30 $\Omega$cm resistivity, which had been oxidised to provide an insulating 100 nm film. Further testing then took place on borosilicate glass wafers as the preferred substrate. A bi-layer lift-off process, using PMGI SF9 and Megaposit SPR-350 photoresists, an EVG 620 mask aligner and MF-319 developer, was then used to produce a base layer pattern on the wafer, on top of which 25 nm of titanium and 100 nm of gold were deposited in the same e-beam evaporation process (Fig. 1a, with the substrate not shown for overall clarity). The photoresist was removed using 1165 stripper.

The lift-off process was repeated with a wide crossover mask design, as in (Fig. 1b), and then an etchant (4:1:8 KI$_2$I$_2$H$_2$O) was used to remove the uncovered gold and to undercut the photoresist, leaving a region of titanium exposed (Fig. 1c). The samples were then placed in an ultrasonic bath in water for 10 s to help remove any remaining gold etchant solution. The exposed titanium was then oxidised using one of the methods described below (Fig. 1d). The lift-off technique was then repeated, with thinner lines than found earlier, thus ensuring that there were no short circuits because of misalignment. 30 nm of platinum was then evaporated, resulting in a small TiTiO$_2$/Pt region being produced (Fig. 1e). Finally, the photoresist was removed as above, which also removed unwanted platinum, completing the diode fabrication process (Fig. 1f).

Initial titanium oxidation involved taking the sample after the gold etching step, and placing it in a temperature controlled humid environment at 100°C for 4 h. To oxidise the titanium in a more controlled manner, the photoresist was removed after the gold etch step and the sample placed in an Oxford Instruments combined PE/RIE system. Here, the sample underwent an initial titanium etch process in RIE mode to remove any native oxide which will have formed on the exposed titanium (100 W, 100 mT, 20 sccm CF$_4$ and 2 sccm O$_2$ for 15 s – RIE mode). This is not strictly necessary as the subsequent plasma oxidation step is a simultaneous etch and oxidation process combined, but it is still performed to improve repeatability between samples by removing the native oxide inherent on any titanium surface, which will have formed in an uncontrolled manner. Without removing the sample from the vacuum, plasma oxidation then took place in plasma etch mode, which resulted in an oxide forming in a controllable way on the surface of the titanium (100–150 W, 500 mT and 100 sccm O$_2$ for 5 min – PE mode). Although the latter process resulted in oxide growth, rather than removal, we will refer to the process as related to machine settings, that is, PE mode.
3. Results: To fully analyse and compare the two different oxidation techniques, time of flight secondary ion mass spectrometry (ToFSIMs) analysis was used to determine both the thickness and the stoichiometry of the resulting oxides. Figs. 2 and 3 show the negative ion analysis of a 4 h furnace oxide and a 100 W PE diode oxide, respectively. As can be seen, neither oxide is dominated by TiO$_2$, as suggested in [6], but rather by sub-stoichiometric TiO. The native furnace oxide has a more complex stoichiometry, in that it consists of significant amounts of various oxides, including the presence of TiO$_2$ and TiO$_3$ at the surface. In contrast, the PE oxide primarily consists of TiO throughout the thickness of the oxide. As a result of the dominant TiO-ions in ToFSIMs analysis of both types of oxide, TiO was chosen as a suitable basis for thickness comparison between each sample.

Along with comparing the two different oxidation methods, the thickness of different power plasmas was of significant interest. As was discussed in [7], the variation in oxide thickness in this process is determined by the plasma power rather than the time. Therefore different diodes were produced using different plasma powers, which resulted in different oxide thicknesses. Fig. 4 shows a profile of the TiO-ions in the following structures: 100, 110, 120 and 150 W plasma diodes and a 4 h furnace diode. As can be seen, there are two peaks present in the TiO-ion trace of the ToFSIMs analysis with a trough region between them. This secondary, lower peak, which occurs away from the surface of the oxide, could occur for a number of reasons. The peak could be caused by a sputtering effect, whereby inconsistencies caused by sputtering of the sample affect the intensity profile, which is unlikely in such a comparatively robust sample (more likely in organic samples). Finally, this second peak could be a real effect caused by the plasma oxidation process. The central trough region in the TiO-trace occurs at the same time as a corresponding hydrogen peak, which could have been caused by hydrocarbon contamination in the RIE. Although interesting, this second peak does not affect the comparison between the resultant trends in oxide thickness, which has been confirmed via transmission electron microscopy (TEM) analysis.

A value of intensity halfway between the peak and the titanium baseline was chosen as a suitable cut-off for comparison between the oxides. As can be seen, all the plasma oxides are thinner than the furnace oxide (6.9 nm), and all are in the region of 5 nm or smaller, which provides an ideal range for conduction mechanism testing, with the aim of achieving electron tunnelling. Furthermore, the thickness of the oxide can be controlled by the power of the plasma, resulting in the ability to tailor the oxide to the requirements of MOM diodes. It is noted (and repeatable) that the oxide thickness reaches a maximum with plasma power, and then falls away with further power increases. It is believed that this is due to the interaction of two simultaneous processes taking place during plasma oxidation; oxide growth and surface etching from plasma bombardment. At low powers, oxidation dominates, with a range of powers causing thickness variations. However, beyond a certain threshold power, etching begins to dominate causing a sudden decrease in oxide thickness without any further power increase. The value of our process is in combining RIE
and a typical current ratio of 1.7, both of which are competitive with the non-uniform and too thick furnace oxide.

### Table 1 Control of titanium oxide thickness with plasma power in PE mode, when compared with a furnace grown oxide

<table>
<thead>
<tr>
<th>Oxide preparation method</th>
<th>Average ToFSIMs thickness measurements, nm</th>
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<tbody>
<tr>
<td>PE 100 W</td>
<td>4.1</td>
</tr>
<tr>
<td>PE 110 W</td>
<td>4.6</td>
</tr>
<tr>
<td>PE 120 W</td>
<td>5.1</td>
</tr>
<tr>
<td>PE 150 W</td>
<td>4.0</td>
</tr>
<tr>
<td>4 h furnace</td>
<td>6.9</td>
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Figure 5 TEM image comparison between oxides in 4 h furnace diode (left) and a PE diode (right) with, from the bottom upwards, the (light) silicon dioxide substrate, e-beam evaporated titanium (with a collimated structure visible), thin titanium oxide layer and finally a (dark) platinum top layer completing the diode structure.

with low power PE of a readily oxidisable metal (i.e. titanium) to etch and then regrow a thin oxide in a controllable manner. The results in Table 1 show that the minimum controllable thickness we have achieved is 4.0 nm. We can produce oxides down to 2 nm thickness; however, the reproducibility needs to be improved. The thickness measurements were confirmed by TEM analysis, which also confirmed the improved uniformity of the plasma oxides over those grown in a furnace, which can be seen from the TEM cross-section images in Fig. 5. Here, defects in furnace oxide are evident in Fig. 5 (left), whereas the uniformity of the PE oxide is apparent in Fig. 5 (right). The electrical results of the furnace diodes exhibited a noticeable variance across a wafer [5], and it is believed that this was because of localised defects in the oxide. However, as can be seen in Fig. 5, less variation in oxide thickness should result in more uniform electrical results for the PE diodes; electrical tests suggest this to be the case. Previous comparisons between different furnace oxidations have been discussed [5], along with initial electrical results under DC test conditions [8]. A figure of merit for these diodes is the zero bias curvature coefficient, which is a measure of the nonlinearity of the diode at a given voltage. Owing to the potential of these devices to act as energy detection and recovery devices, the aim is to have them operate without an applied bias. Previous results have found that furnace diodes have a typical zero bias curvature coefficient of 3.1 V⁻¹, and a typical current ratio of 1.7–3.5. By comparison, initial results on these plasma fabricated diodes give typical curvature coefficients of 2.8 V⁻¹ and current ratios of 1.7, both of which are competitive with the non-uniform and too thick furnace oxide.

### 4. Conclusions

Titanium oxides have been produced using a combination of reactive ion etching and plasma oxidation; these oxides are thinner and more uniform than previous furnace oxides. Furthermore, they are sufficiently thin for high-speed electron tunnelling to occur and the thickness can be controlled by plasma regrowth power. This latter conclusion has been confirmed by ToFSIMs, whose summary can be seen in Table 1. Further tests are ongoing to assess the AC capability of diodes fabricated by this plasma-assisted technique, where the much thinner oxide is expected to lead to a high frequency performance with the uniformity giving the opportunity for one conduction mechanism, for example, direct electron tunnelling, to dominate. Analysis of these AC results is ongoing. This thin, uniform range of oxides can then be used to tailor high-speed MOM diodes for use as rectification components in ‘rectenna’ arrays for the detection and recovery of infrared radiation.

### 5. Acknowledgments

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### 6 References