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**Influence of microstructure on electrical properties of diluted GaN_xAs_{1-x}
formed by nitrogen implantation**

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ABSTRACT

Structural studies of GaAs implanted with N or co-implanted with other elements showed that, in addition to typical post-implant defects, small voids were present in the implanted region in such materials. Comparison of the microstructure found in these layers with electrical results indicates that these voids are responsible for the low activation efficiency of N implanted into GaAs. The results show that the N-induced enhancement of the donor activation efficiency can be achieved only in void-free region of the implanted sample.

It has been demonstrated recently that nitrogen (N) implantation into GaAs can be applied to produce thin films of diluted $\text{GaN}_x\text{As}_{1-x}$ alloy.¹ Since introducing even a small amount of N into GaAs significantly modifies its conduction band structure, causing considerable reduction of the bandgap energy and a large increase of the electron effective mass,²⁻⁴ dilute $\text{GaN}_x\text{As}_{1-x}$ alloys seem to be promising materials for a variety of applications in long wavelength optoelectronic devices and high efficiency solar cells.⁵⁻⁷ Recently it has been suggested that dilute $\text{GaN}_x\text{As}_{1-x}$ layers can be used in the achievement of low-resistance, nonalloyed ohmic contacts to n-type GaAs.⁹ This potential application arises from the increase of the maximum free electron concentration in n-type $\text{GaN}_x\text{As}_{1-x}$ due to the nitrogen-induced modification of the conduction band.⁸⁻⁹ In fact, a large increase in the electrical activation of sulfur (S) co-implanted with nitrogen in GaAs has been observed.⁹ However, this increase is observed only in the near-surface region and the mechanism leading to such behavior is not yet clear.

Another not fully understood problem associated with the formation of dilute $\text{GaN}_x\text{As}_{1-x}$ alloys by N implantation is the low N activation efficiency. It was observed that after post-implantation annealing, only a small fraction of the implanted N remains in “active” group V sub-lattice sites. For GaAs implanted with N an activation efficiency of about 10-15% has been measured.^{1,10} Restoring the local stoichiometry by co-implanting Ga with N in GaAs resulted in a factor of two increase in the N activation efficiency.¹⁰ The low N activation efficiency indicates that most of the implanted N atoms exists in some “inactive” form. Here in this letter, we investigate: (1) the nature of the “inactive” N in $\text{GaN}_x\text{As}_{1-x}$ layers formed by N implantation; and (2) the mechanism causing an

increase of electrical activation only in the near surface region induced by N implantation in S and N co-implanted GaAs samples.

Two types of samples were studied by transmission electron microscopy (TEM) in this work: (i) N and Ga+N co-implanted GaAs and (ii) S and S+N co-implanted GaAs. In the former case the purpose was to study the relationship between defect microstructure and the low activation efficiency of N in the $\text{GaN}_x\text{As}_{1-x}$ layers. In the latter set of samples effects of the microstructure on the reduced electrical activation of S in S and N coimplanted GaAs were studied. Multiple energy ion implantation was carried out in all cases forming layers of $\sim 0.2\text{-}0.4\ \mu\text{m}$ thick with uniform concentrations of the implanted species. The parameters of the samples are listed in Table I. The implanted samples were annealed by rapid thermal annealing (RTA) in a flowing N_2 ambient with the sample surface covered by a “dummy” GaAs wafer. Cross-sectional TEM specimens were prepared by the standard method of mechanical thinning followed by ion milling. TEM studies were carried out using a TOPCON 002B microscope operated at 200 kV.

TEM micrographs obtained for the first set of samples (N and N+Ga) after RTA at 800°C for 10sec. are shown in Fig.1. In the sample implanted with N only a band of dislocation loops, extended from about $0.1\ \mu\text{m}$ down to about $0.5\ \mu\text{m}$ below the surface. In the N and Ga co-implanted sample the density of observed structural defects was much larger due to the greater damage caused by the heavier Ga atoms. In the first part of this highly defective layer, located also at depths between about $0.1\ \mu\text{m}$ and $0.5\ \mu\text{m}$ from the surface, a high density of dislocations, large dislocation loops and stacking faults were present. Below this region in the area down to about $1\ \mu\text{m}$ from the surface a large

density of small dislocation loops was observed. Defects found in both of these samples are typical implantation damage defects.¹¹⁻¹²

In addition to these typical implantation induced defects, void-like defects were also present in both samples (see Fig.1). In the GaAs sample implanted with N only a layer containing a very high density of small voids, with an average size of about 2-3 nm, started just below the surface and continued to a depth of about 0.6-0.7 μm . Such void-like defects are not observed in samples implanted with S only (see below) and are present only in N implanted samples. This strongly suggests that these voids are related to N and are likely formed by the segregation of N during annealing. Presence of these voids (or N bubbles) may account for the low N activation efficiency in these samples: ~15% for N only and 30% for Ga+N implanted GaAs samples after RTA at 800°C. For the samples implanted with N only after RTA at 950°C only negligible amounts of N were found to remain in active sites.¹⁰ It is worth mentioning here, that such thermally induced formation of voids have been previously reported for GaAs and other semiconductors implanted with gas atoms.¹¹⁻¹⁵

In the sample co-implanted with N and Ga the voids were larger (with an average diameter of about 5-6 nm) but their density was much lower. They were located in a relatively narrow layer at depths between about 0.1 and 0.4 μm . These two effects indicate that less N is trapped in the voids and could account for the measured higher (by a factor of two) N activation and thermal stability in this sample. The formation of voids during annealing as, shown by the TEM results on GaAs implanted with N or co-implanted by N and Ga, appears to be responsible for the very low activation efficiency of N implanted into GaAs resulting in much lower than expected modification of the

conduction band. It should also be pointed out that no noticeable N redistribution was observed by secondary ion mass spectrometry for this implantation dose even after annealing at 900°C for 20 s, indicating that the "inactive" N is incorporated in the voids forming N "bubble"-like structures in these samples

Free electron concentration profiles measured by electrochemical capacitance voltage (ECV) from samples implanted with S and co-implanted with S and N and annealed at 945°C for 10 s are shown in Fig.2. The calculated, as-implanted S and N atomic distributions are also shown in the figure. The most striking difference in the electron concentration profiles between the S only and (S+N) samples shown in Fig. 2 is the much enhanced (almost an order of magnitude) electron concentration in the (S+N) sample in a narrow region ($<0.1\mu\text{m}$) near the surface. In addition, there exists a region at a depth of about 0.2 μm below the surface that showed a minimum in the electron concentration for both cases. In the case of S and N co-implanted samples this minimum was much deeper and broader.

Bright field TEM images obtained from these two materials are shown in Fig.3a and Fig.3b. The main structural feature observed in both samples (except for significant damage of the surface) was a band of defects present at a depth of about 0.2 μm below the surface. These defects were dislocation loops located on $\{111\}$ planes surrounding extrinsic stacking faults (Fig.3d). In both samples these bands were about 0.1 μm wide. In samples implanted only with S the band was slightly broader. The average loop size was also smaller in this sample. It was about 10 nm in contrast to about 15 nm measured for the S and N co-implanted sample. This band of dislocation loops is a typical feature in implanted and then annealed GaAs. In addition to this band of dislocation loops, in the

sample implanted only with S a narrow band of tiny defects was observed at a depth of about 0.13 μm below the surface. High resolution studies of these defects suggests that they are stacking fault tetrahedra (Fig.3e). Such defects have been previously reported in implanted GaAs.¹⁶⁻¹⁷

In the S and N co-implanted sample there are pits observed at the surface formed possibly as a results of too high an annealing temperature or stacking fault formation. In this sample instead of a band of stacking fault tetrahedra a broad layer containing a high density of small voids (of an average size of about 4-5 nm) was observed (Fig.3f), similar to those shown in Fig. 1. Most of these voids were concentrated in a layer extending from $\sim 0.1 \mu\text{m}$ to $\sim 0.3 \mu\text{m}$ below the surface. Their concentration abruptly faded outside this area. The location of these voids correlates very well with the region of reduced electron concentration measured by ECV. In the sample implanted only with S the dip in the electron concentration profile correlates well with the location of the observed band of dislocation loops. We believe that a significant fraction of the S implanted into this region becomes inactive by accumulating around the dislocation loops. This mechanism is also partially responsible for the reduced electrical activation of S in the co-implanted sample. However, in this case the presence of voids is an even more important mechanism in reducing electrical activity of S. We assume that, these voids are formed as agglomerates of vacancies filled with N and act as defect centers compensating electrical activity of S donors. This argument is strongly supported by the observed very large activation efficiency of S donors in the void-free region within the $\sim 0.1\mu\text{m}$ near the surface.

In conclusion, transmission electron microscopy studies of GaAs implanted with N showed that besides the typical implantation induced structural defects voids are formed in the material. These results suggest that the voids are filled with N and can be responsible for the extremely low activation efficiency of N implanted into GaAs. This tendency for N segregation into voids is a serious problem for production of dilute $\text{GaN}_x\text{As}_{1-x}$ by N implantation. It is shown that large N-induced enhancement of the donor activation efficiency can only be realized in the void-free region.

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Table I. Detailed information on the N implantation conditions on the various samples.

| sample | | Impurity concentration (cm^{-3}) | Implanted layer thickness (μm) |
|----------|----|---|---|
| Set (i) | N | 4×10^{20} | 0.5 |
| | Ga | 4×10^{20} | 0.5 |
| Set (ii) | S | 6×10^{19} | 0.2 |
| | N | 3.5×10^{20} | 0.35 |

Figure Captions

Fig.1. TEM micrographs of GaAs implanted with N [(a), (c), and (e)] and co-implanted with N and Ga [(b) and (d)].

Fig.2. ECV measured net donor concentration profiles for the GaAs samples implanted with S alone and S+N after RTA at 945 °C for 10 s. The calculated atomic profiles for both the implanted S and N are also shown.

Fig.3. TEM micrographs of GaAs implanted with S [(a), (c), (d) and (e)] and co-implanted with S and N [(b) and (f)].

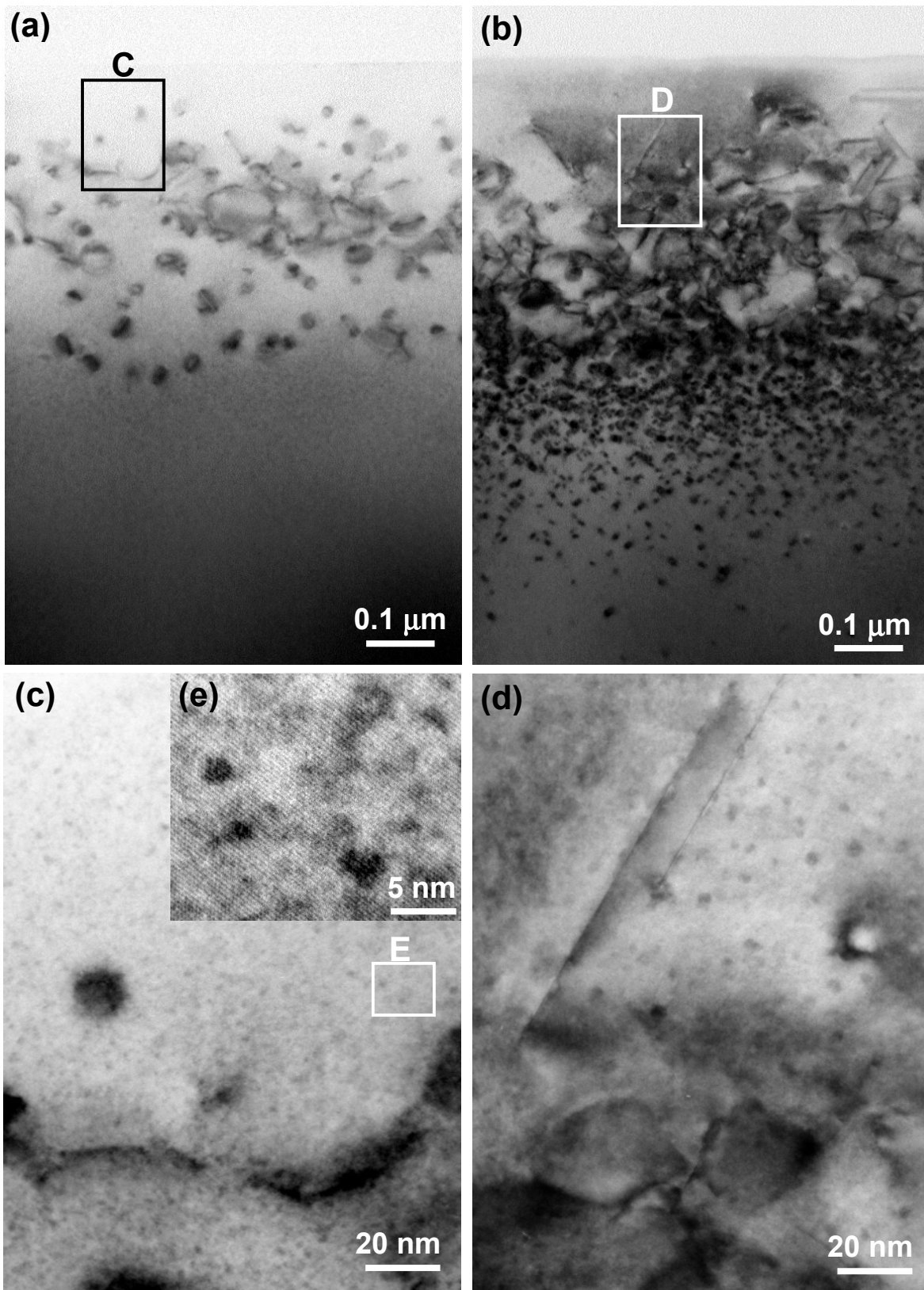


Fig.1, J. Jasinski, L01-1278

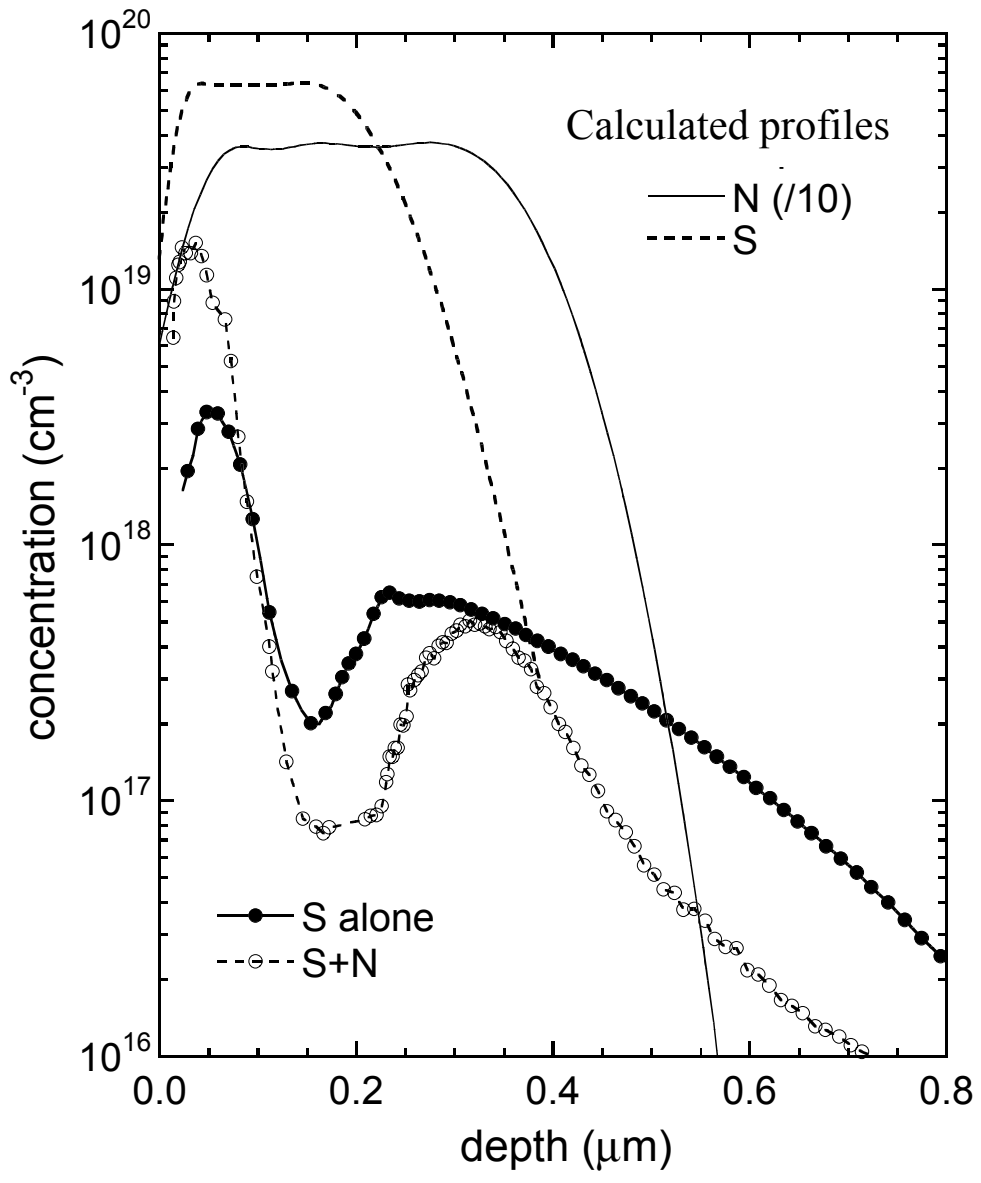


Fig.2, J. Jasinski, L01-1278

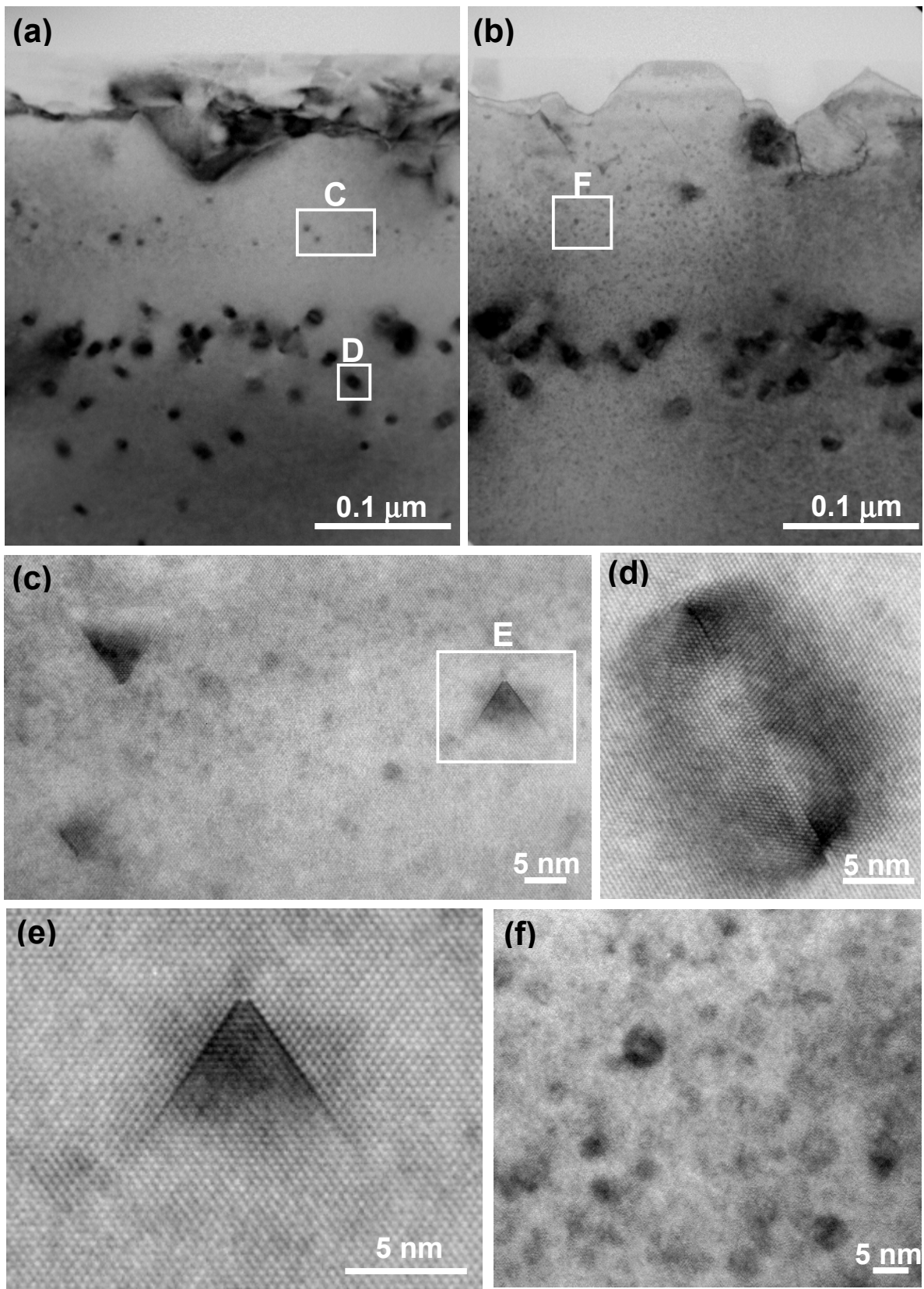


Fig.3, J. Jasinski, L01-1278