

A **Microstructural** Comparison of the Initial Growth of **AlN** and **GaN** Layers on Basal Plane Sapphire and **SiC** Substrates by Low Pressure **Metalorganic** Chemical Vapor Deposition

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The initial growth by low pressure **metalorganic** chemical vapor deposition and subsequent thermal annealing of **AlN** and **GaN** **epitaxial** layers on **SiC** and sapphire substrates is examined using high resolution transmission electron microscopy and atomic force microscopy. Growth under low pressure conditions on sapphire substrates is significantly different from that reported for conventional (atmospheric pressure) conditions. Smooth, single crystal **AlN** and **GaN** layers were deposited on sapphire in the initial low temperature (600°C) growth step. **Interfacial** bonding and not lattice mismatch was found to be the determining factor for obtaining good **crystallinity** for the **epitaxial** layers as indicated by the growth results on **SiC** substrates.

The III-N heteroepitaxially grown semiconductors have gained technological importance recently due to advances in the growth techniques.¹ These advances have resulted in improved crystalline quality for the epitaxial layers enabling the fabrication of optoelectronic devices. Much work however remains to be done in developing an understanding of the factors influencing the growth of these layers. The substrate of choice for the growth is basal plane (0001) sapphire. Sapphire substrates are relatively easy to clean, are available with good crystalline quality and have excellent high temperature stability. The main drawback to using sapphire is its large lattice mismatch with the epitaxial nitride layer. The observed orientation relationship of epitaxial GaN with the sapphire substrate is the following: $(0001)\text{GaN} \parallel (0001)\text{Al}_2\text{O}_3$ and $[1\bar{1}00]\text{GaN} \parallel [1\bar{2}10]\text{Al}_2\text{O}_3$. The lattice mismatch $(\frac{d_{\text{GaN}} - d_{\text{Al}_2\text{O}_3}}{d_{\text{GaN}}})$ for this orientation is about 14%. The poor crystallinity of GaN layers grown directly on sapphire substrates has been attributed to this large lattice mismatch.

Using reactive molecular beam epitaxy, the growth of an intermediate (buffer) layer of AlN between the GaN and the sapphire was first shown to significantly improve the optical and electronic properties of the overgrown GaN film by Yoshida *et al.*³ Extensive work by Akasaki's group^{2,4,5} using atmospheric pressure metal organic chemical vapor deposition (APMOCVD) confirmed these results and an optimized recipe was developed by them for the growth of high quality GaN films. This recipe consisted of a two-step process in which a thin (~20 nm) AlN buffer layer was grown at low temperature (~600°C) on the sapphire substrate in the first step, the substrate temperature was then raised (~1000°C) and the GaN layer growth was initiated in the second step.

Recently, high quality 6H SiC substrates have become commercially available. SiC has an in-plane lattice constant (0.358 nm) similar to that of AlN (0.354 nm) and is therefore more closely lattice matched to GaN than sapphire. The expectation in using SiC substrates is that the lower lattice mismatch will result in improved crystallinity for

the heteroepitaxial GaN layers. However, obtaining clean substrate surfaces prior to growth appears to be the major obstacle to the achievement of good quality epitaxy.⁶

The epitaxial growth technique used in this study was low pressure metalorganic chemical vapor deposition (LPMOCVD). The ambient pressure in the growth reactor was maintained at 76 Torr. Under these conditions, when AlN buffer layers were grown on sapphire substrates prior to the growth of epitaxial nitrides using a recipe similar to that of the Akasaki group, the AlN layers were observed to be composed of single crystal columns with pyramidal tops (Fig. 1). This result differs from their APMOCVD results which showed that specular epitaxial surfaces could be obtained by using AlN buffer layers. In this work, by using GaN buffer layers instead, planar interfaces were achieved with the overgrown layer (Fig. 2). Once again this result contrasts with the APMOCVD results which clearly showed a rough surface morphology for GaN layers grown directly on sapphire. Thus the growth behavior under low pressure conditions appears to be significantly different from that at atmospheric pressure. Since no data was available on the initial growth behavior of AlN and GaN under low pressure conditions, the following growth study was initiated, in which the growth behavior of thin layers (~20 nm) of GaN and AlN on sapphire and SiC substrates was observed.

Structural characterization was performed on eight initial growth samples produced using a growth matrix consisting of two epitaxial layers (GaN, AlN), two substrates (Al₂O₃, SiC) and two process conditions (as grown, post anneal). Basal plane (0001) sapphire and SiC substrates were used. The substrates were cleaned using organic solvents followed by etching with dilute acids. The substrates were subsequently introduced into the growth reactor and heated to 1000°C prior to lowering the temperature of the susceptor to the growth temperature of 600°C. The source gases used were ammonia, triethylaluminum and triethylgallium. Epitaxial layers nominally 20 nm thick were grown directly on the substrates at 600°C. The samples were subsequently removed from the reactor and cleaved in two. One of the cleaved pieces from each

sample was then annealed at 1000°C for thirty minutes under flowing NH_3 . Additional samples were grown separately under identical conditions and subjected to sputter Auger to confirm the presence of GaN and AlN respectively.

The samples were characterized using high resolution transmission electron microscopy (HRTEM) using a Topcon 002B 200kV electron microscope and atomic force microscopy (AFM) using a Digital Nanoscope III scanning probe microscope with silicon nitride tips. For the HRTEM observations cross-sectional specimens were prepared from the samples using mechanical thinning and argon ion milling to achieve electron transparency. The crystallinity and local surface roughness of each film was determined from the cross-sectional HRTEM observations.

The surface morphology of each sample was obtained from $1\mu\text{m} \times 1\mu\text{m}$ AFM scans which generated 512×512 pixel images. R.m.s roughness measurements and height histograms were taken from 128×128 pixel ($0.25\mu\text{m} \times 0.25\mu\text{m}$) areas of the smoothest regions of the scans, in order to ensure that large scale substrate roughness did not affect the values. AFM imaging of the nitrides was problematic: the hardness of the material together with high angle faceting in many cases caused *extreme* tip wear even at the lowest contact forces. Scans were repeated many times with fresh tips until consistent results were obtained. However, the absence of features showing clear crystallographic faceting in the scans is most likely due to blunting of the tips during the initial stages of contact.

Cross-sectional HRTEM micrographs of AlN buffer layers grown on sapphire before and after anneal are shown in Figs. 3a and b respectively. The as-grown layer appears to be mostly single crystal in nature and having a smooth surface (Fig. 3a). The coverage of the sapphire substrate surface appears essentially continuous and individual islands could not be distinguished. After annealing at 1000°C however, the AlN continues to remain single crystal in nature but with the formation of some facets (see arrow) similar to those observed in the thicker buffer layers (Fig. 1). Representative AFM

micrographs showing the surface morphology of the two layers is shown in Figs. 4a and b. Both layers have mostly smooth surfaces (r.m.s roughness value 0.55 nm) with island like features.

The AlN buffer layer grown on the SiC substrates has poor crystallinity and a rough surface morphology as revealed by the cross-sectional HRTEM observations (Fig. 5a). Upon thermal annealing (Fig. 5b), however, there appears to be very little improvement in the surface roughness. The AFM results support the HRTEM observations, as can be seen in Figs. 6a and b. The as-grown AlN layer contains a higher density of islands and a higher r.m.s. roughness (0.94 nm) (Fig. 6a) as compared to AlN grown on sapphire (Fig. 4a). After annealing, there is a slight reduction in the r.m.s. roughness (0.76 nm) of the AlN/SiC layer without a significant change in the surface morphology.

The GaN layer grown on sapphire at 600°C appears to have a smooth surface morphology and a uniform thickness of 17 nm (Fig. 7a). The layer is single crystal in nature, with an extremely high density of structural defects (dislocations and stacking faults). After annealing, the thickness of the GaN layer was observed to be ~3 nm in the region of HRTEM observation. Therefore, a significant reduction in the thickness appears to have taken place as a consequence of the annealing. The AFM results were crucial to explaining this apparent anomaly. The surface morphology of the as-grown GaN layer is seen in Fig. 8a. As can be seen in the micrograph, the GaN has a smooth surface (r.m.s. roughness = 0.45 nm) with a few large islands being present. On annealing the GaN however, an Ostwald ripening type behavior is seen, with several large islands being formed (r.m.s. roughness = 1.16 nm), accompanied by a reduction in the original layer thickness.

Growth of GaN on SiC at 600°C results in the formation of a heavily defective single crystal layer (Fig. 9a). Upon annealing however, no trace of the layer was seen in the region of HRTEM observation (Fig. 9b). The AFM results confirm this surprising

result. Fig. 1 0a shows an **islanded** as-grown GaN layer (r.m.s. roughness = 0.5 nm) and after annealing (Fig. 10b) a featureless surface is observed (r.m.s. roughness = 0.33 nm), possibly corresponding to the substrate surface.

The results from this study are in contrast with those obtained for atmospheric pressure by Koide et al.⁴ After the low temperature deposition step, they found the AlN layer to be mostly amorphous with the presence of **microcrystallites** with large disorientation. In this study, the as grown AlN on sapphire was single crystal in nature and did not contain large amorphous regions nor **microcrystallites** with large disorientation. This effect could be due to a more **efficient** "seeding" of the growing crystal on the sapphire surface under low pressure conditions. The columnar structure of the thick AlN buffer layer (Fig. 1) indicates an island type initial growth mode. The relaxation of the extremely high lattice mismatch strain with the substrate can be expected to be different for each island, resulting in the formation of structural defects delineating the boundaries of the islands. The AlN/Sapphire initial growth sample however, appears to indicate that individual islands of AlN if formed, could have a high rate of lateral growth, **leading** to coalescence at a much lower thickness than 20 nm. The formation of facets is not **well** understood and could possibly be explained by a combination of surface energy and strain relaxation arguments.

The poor **crystallinity** of the AlN films grown on SiC substrates is surprising. The expectation that a lower lattice mismatch with the substrate alone would improve **epitaxy** was obviously disproved. Instead, other factors such as interracial bonding are probably **key** to determining how well the deposited layer grows on the substrate. The rough surface morphology and the presence of large amorphous regions are indicative of seeding of the growing crystal only in local areas, leading to dissimilar growth rates between *the* seeded and unseeded parts of the **film**. The improvement in **crystallinity** with annealing shows that it is possible to convert the amorphous regions by lateral solid phase **epitaxy** from adjacent crystalline areas. The slight improvement in surface morphology is

indicative that surface diffusion rates are not high enough at the annealing temperature for either planarization or faceting to occur.

The growth of a smooth, single crystal film of GaN directly on sapphire also differs from the earlier APMOCVD results. The suppression of large island formation as observed under atmospheric conditions could be due to the improved seeding on the sapphire substrate under low pressure conditions. As a result, a higher density of islands is probably formed on the substrate, subsequently leading to rapid coalescence of these islands and a quasi two dimensional growth mode. The presence of an extremely high density of structural defects in the as grown layer could be evidence for such a growth mode. On annealing however, both bulk and surface diffusion become greatly enhanced causing the improvement in film crystallinity and roughening of the surface due to an Ostwald Ripening type process.

The crystallinity and surface roughness of the GaN layer grown directly on SiC is superior to that for the AlN. This is probably due to the higher mobility of the Ga species on the SiC substrate. Although the GaN is single crystal in nature there is a high density of structural defects. As in the case of AlN, it is evident that interracial bonding plays a crucial role in the epitaxy of GaN from the results obtained after annealing. Both the HRTEM and AFM results show the layer to have almost completely desorbed from the surface of the SiC after annealing. Weak interracial bonding is the most likely cause for this result.

In summary, the initial growth of AlN and GaN layers on SiC and sapphire substrates and their response to thermal annealing was examined. It was found that under low pressure conditions, the growth behavior of these layers is distinctly different from that under atmospheric pressure conditions. Single crystal and not amorphous layers of AlN and GaN were grown on sapphire in the low temperature growth step. Interracial bonding appears to have a stronger role in determining the quality of epitaxy of these layers than lattice mismatch. Epitaxy on SiC substrates of both AlN and GaN was poorer

than on sapphire. Surface diffusion at annealing temperatures is higher for **GaN** than for **AlN**.

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Fig. 2 Cross-sectional TEM micrograph showing a planar GaN buffer layer grown on sapphire as evidenced by the interface with the overgrown layer (SPSL).

Fig. 3 Cross-sectional TEM micrographs of AlN/sapphire layers (a) as grown at 600°C and (b) after anneal at 1000°C.

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Fig. 10 AFM micrographs showing the surface morphology of GaN/SiC layers (a) as grown at 600°C and (b) after anneal at 1000°C.

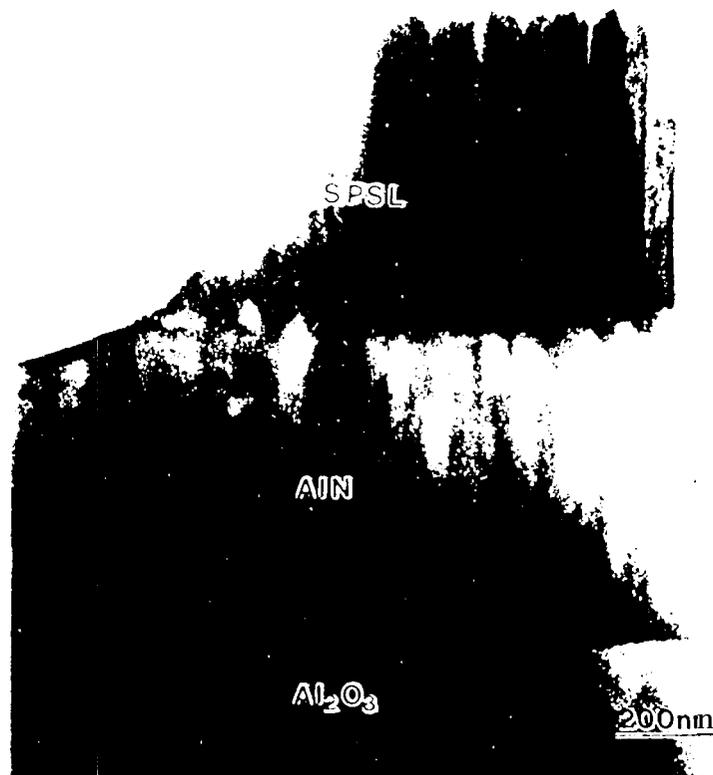


Fig. 2

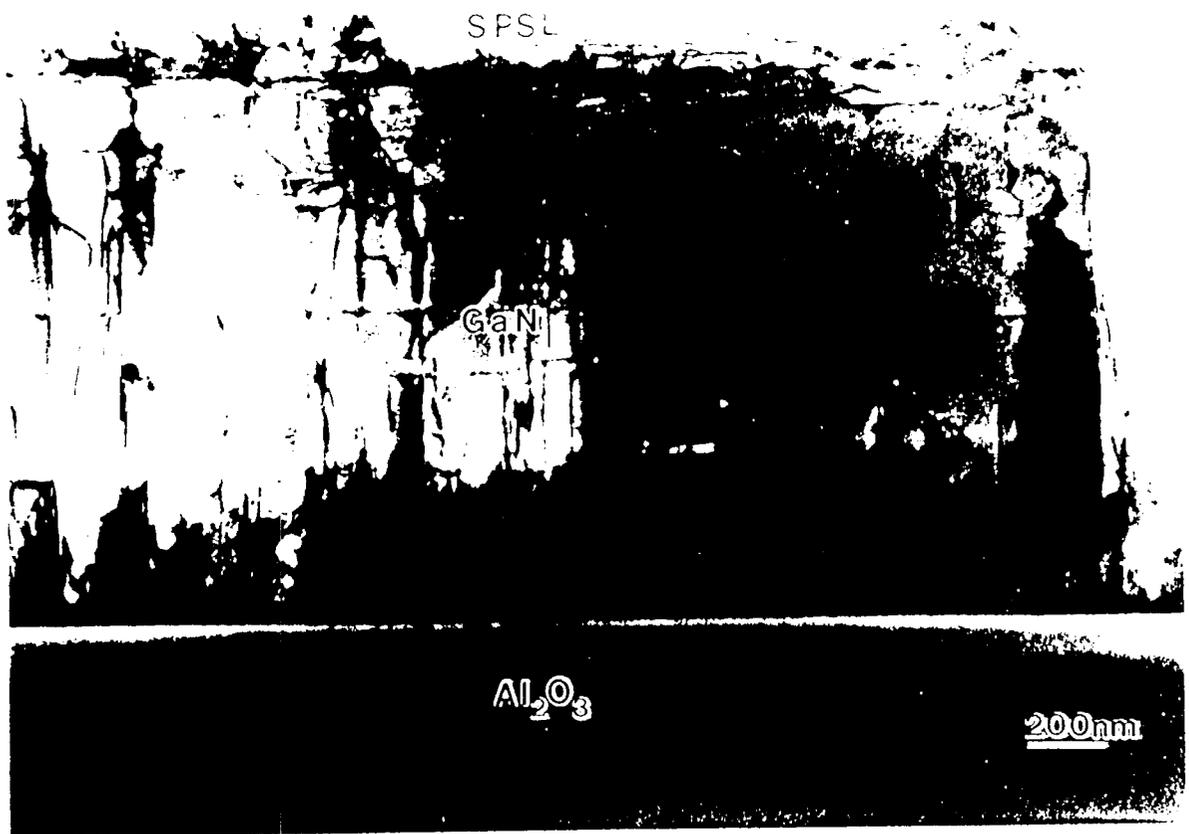


Fig. 3a and b



Fig. 3a



fig. 3b

Pg. 4a

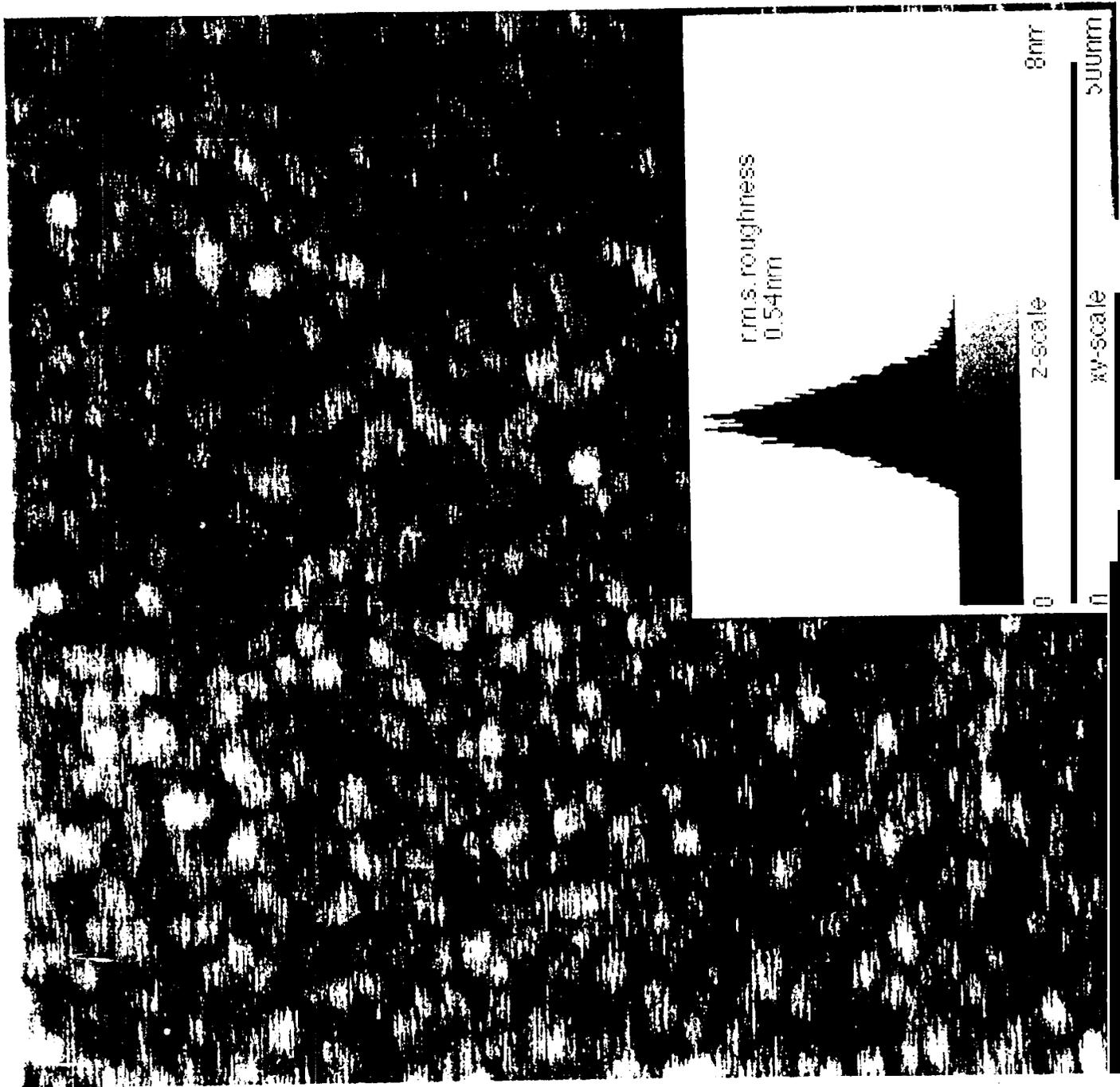
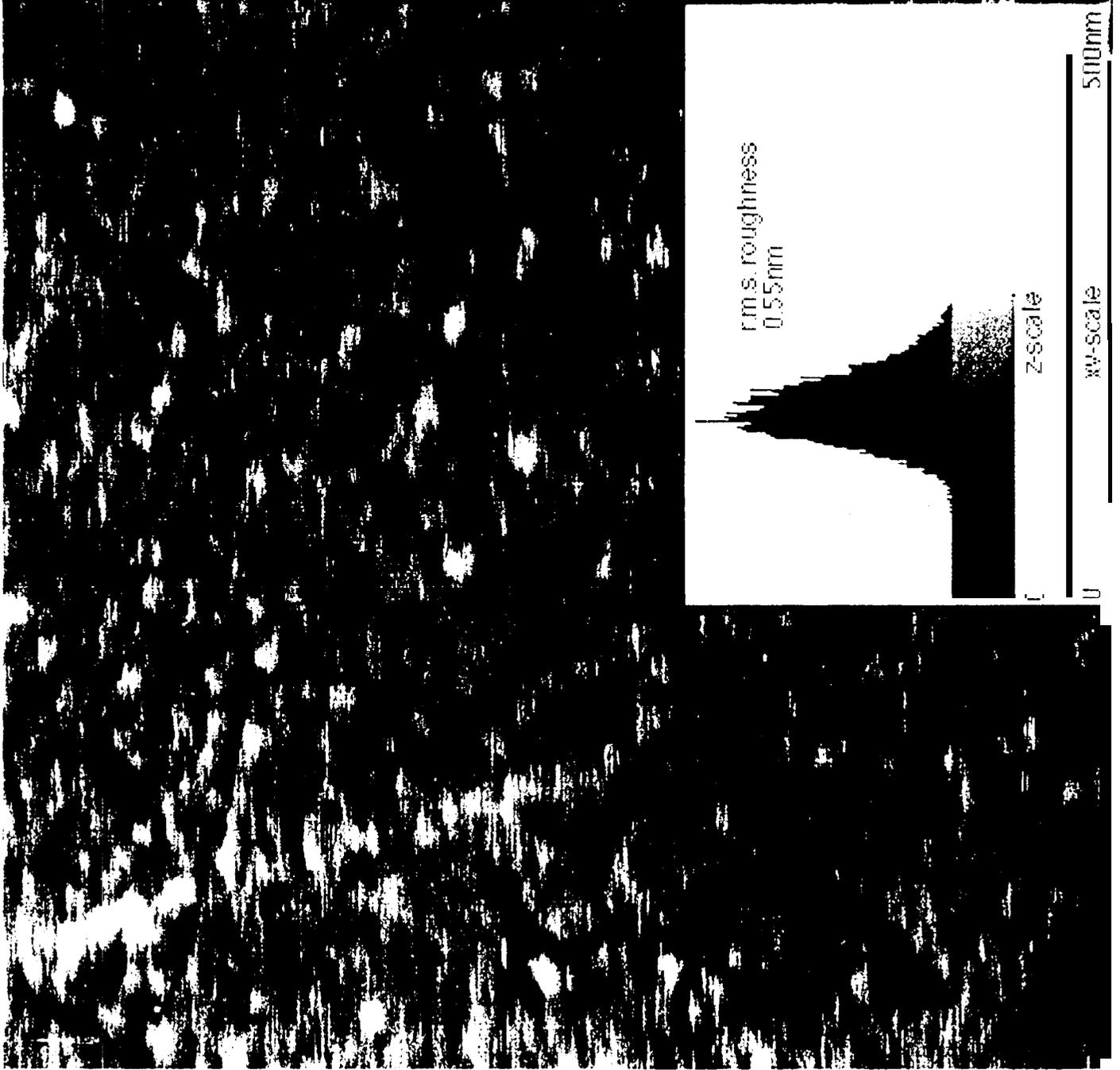
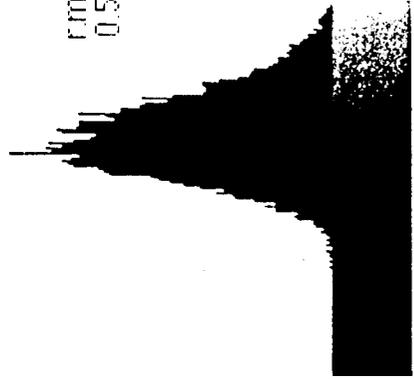


Fig 4b



r.m.s. roughness
0.55nm



500nm

xw-scale

z-scale

Fig. 5a and b



Fig. 5a



Fig. 5b

Fy 69

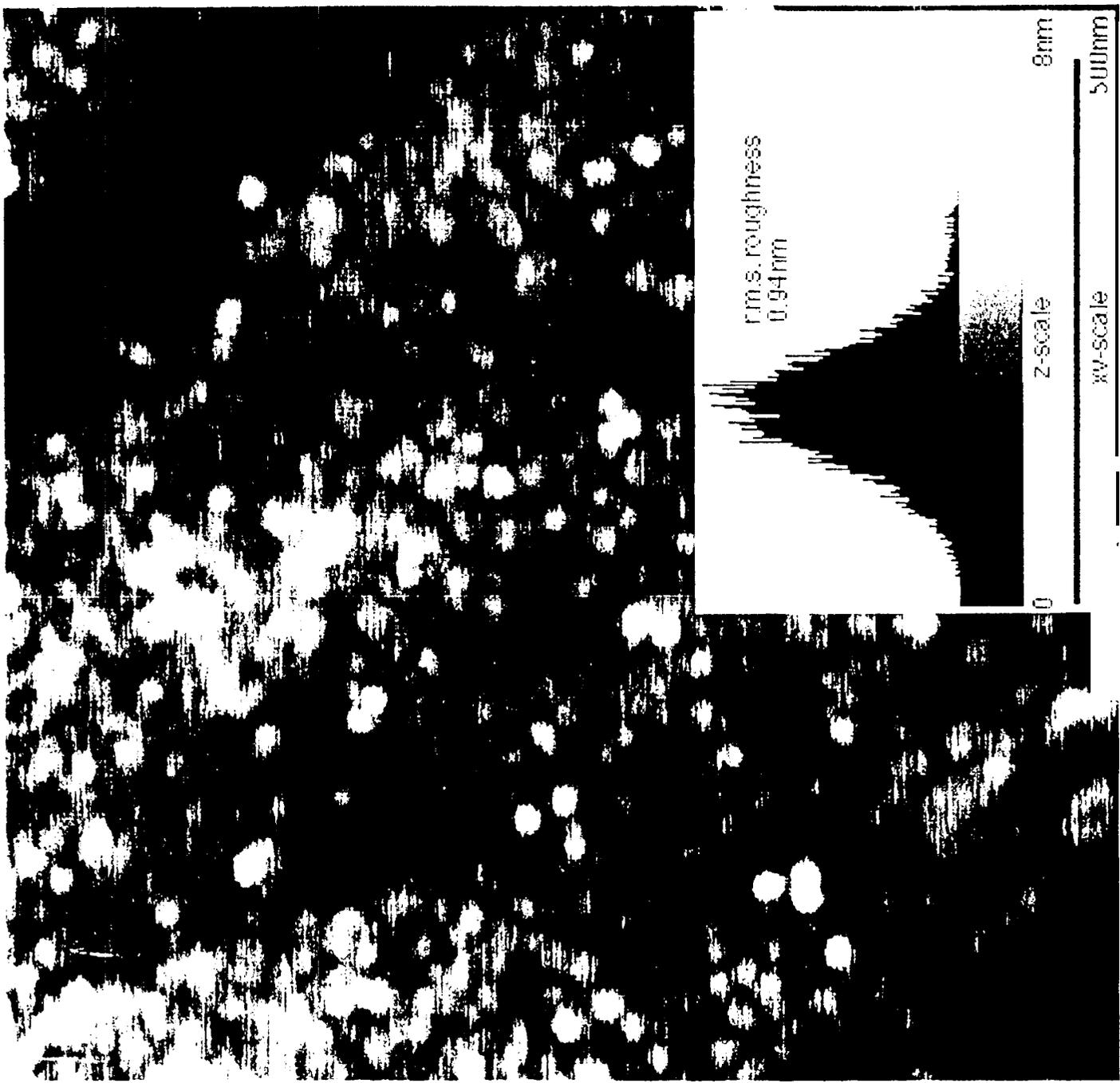


Fig. 6b

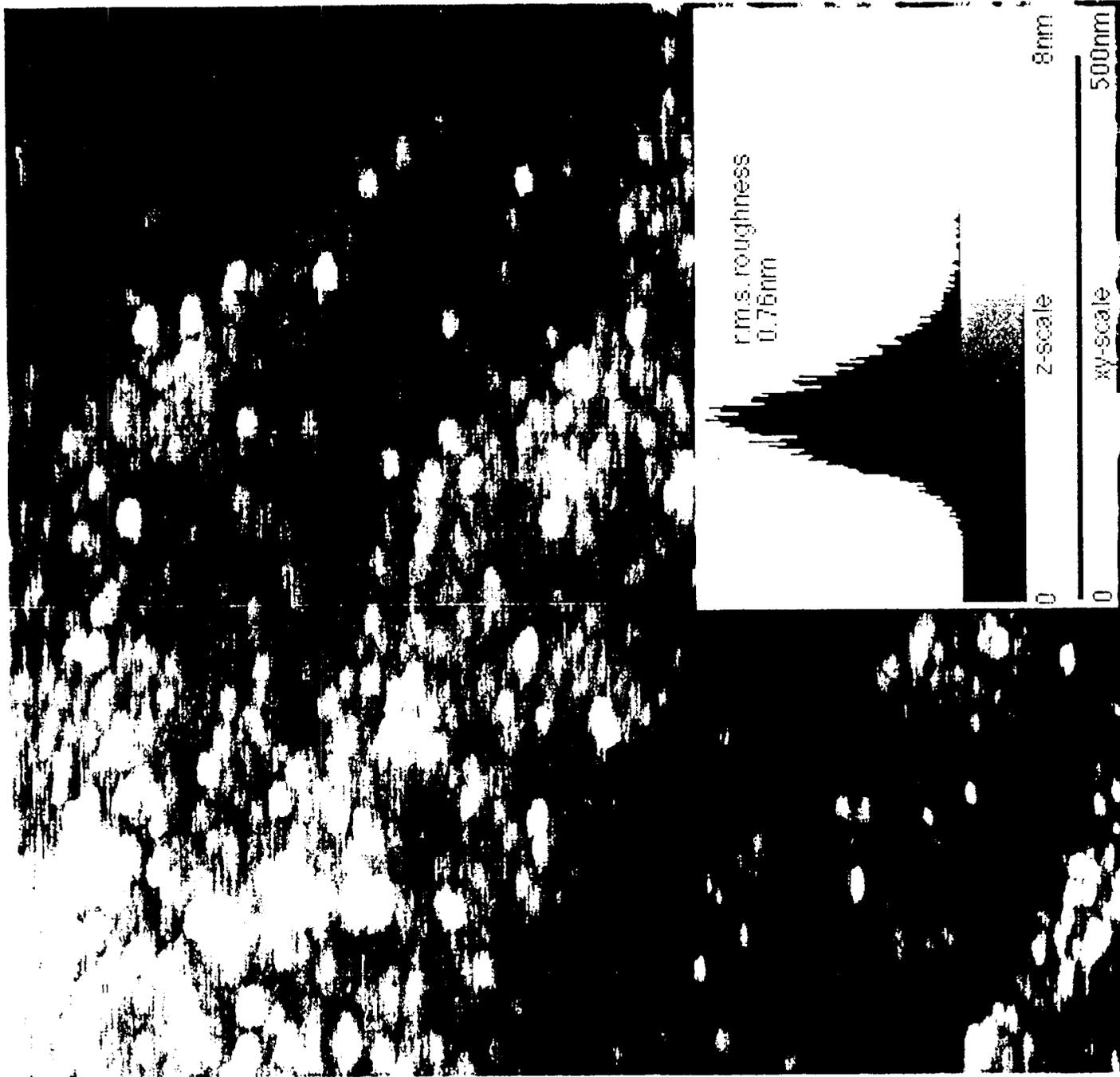


Fig. 7a and b.

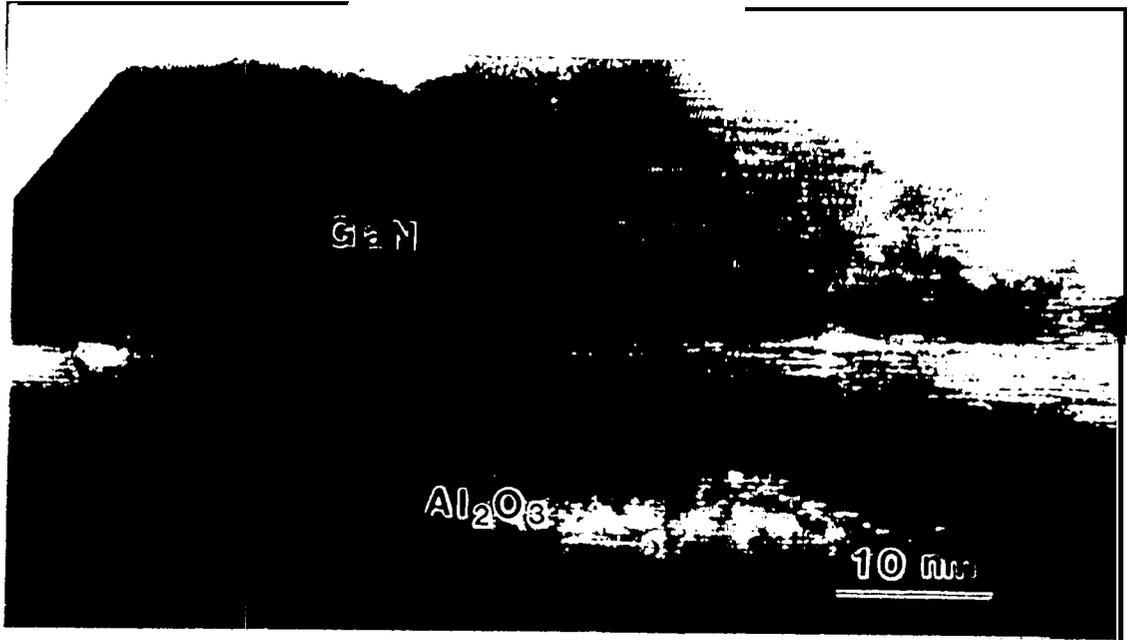


Fig. 7a

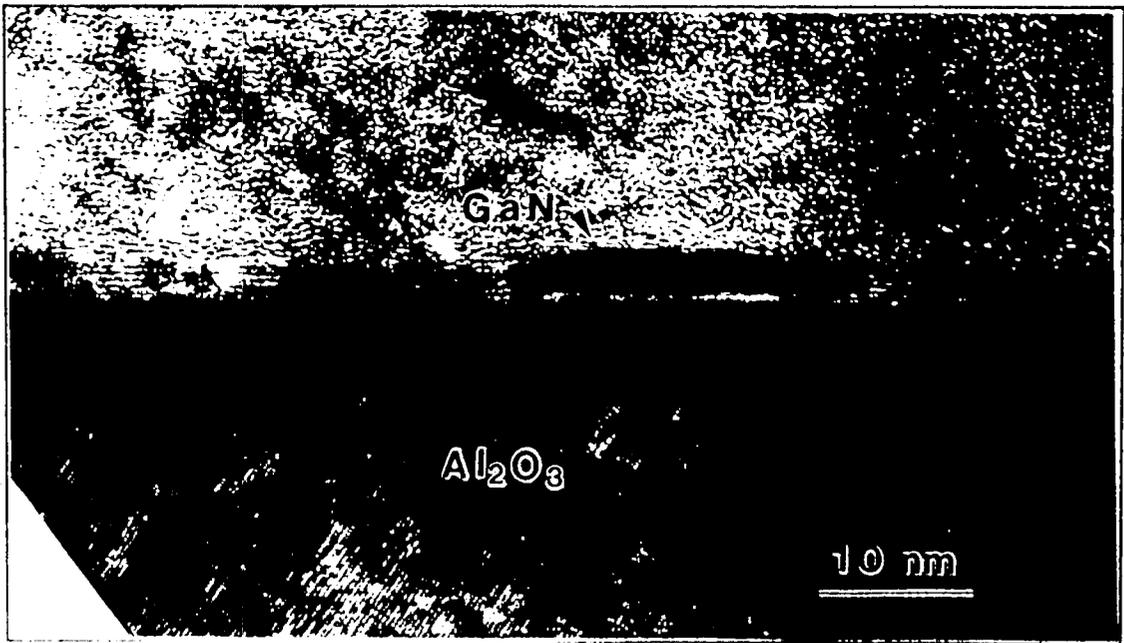
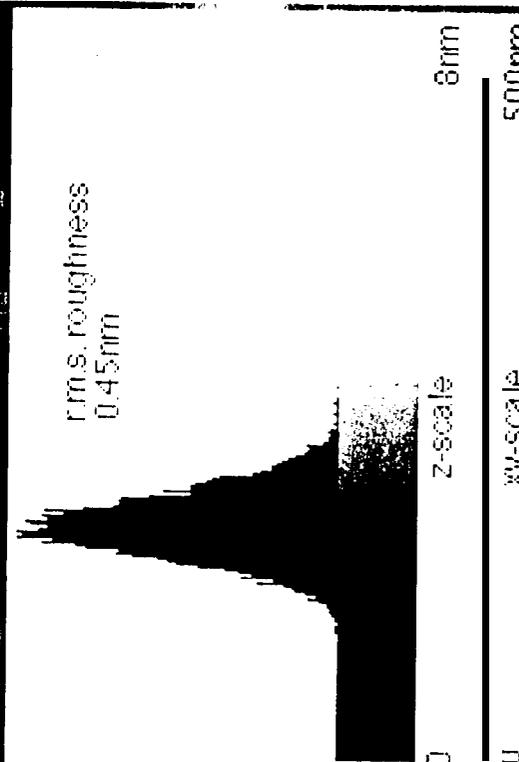
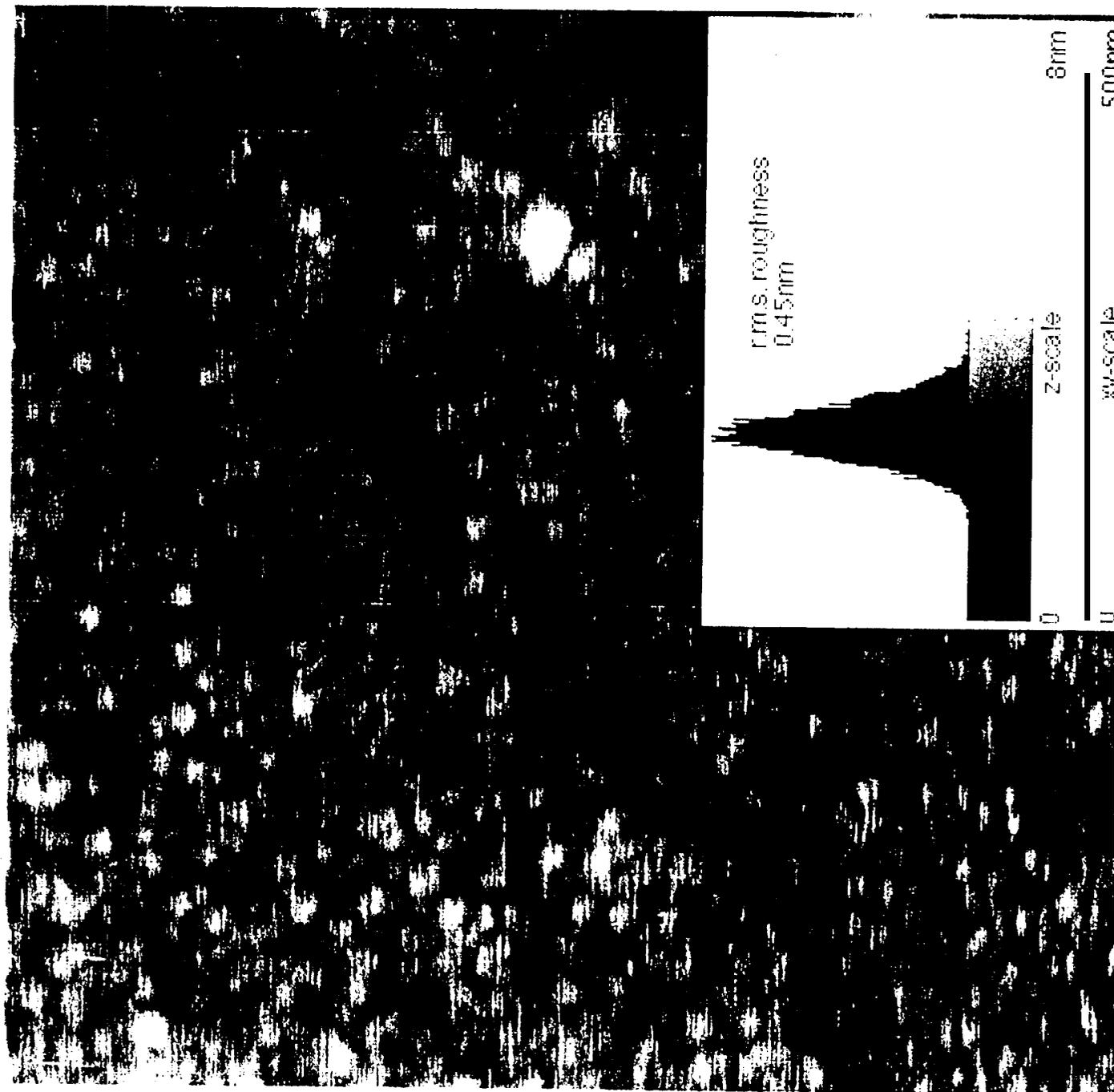
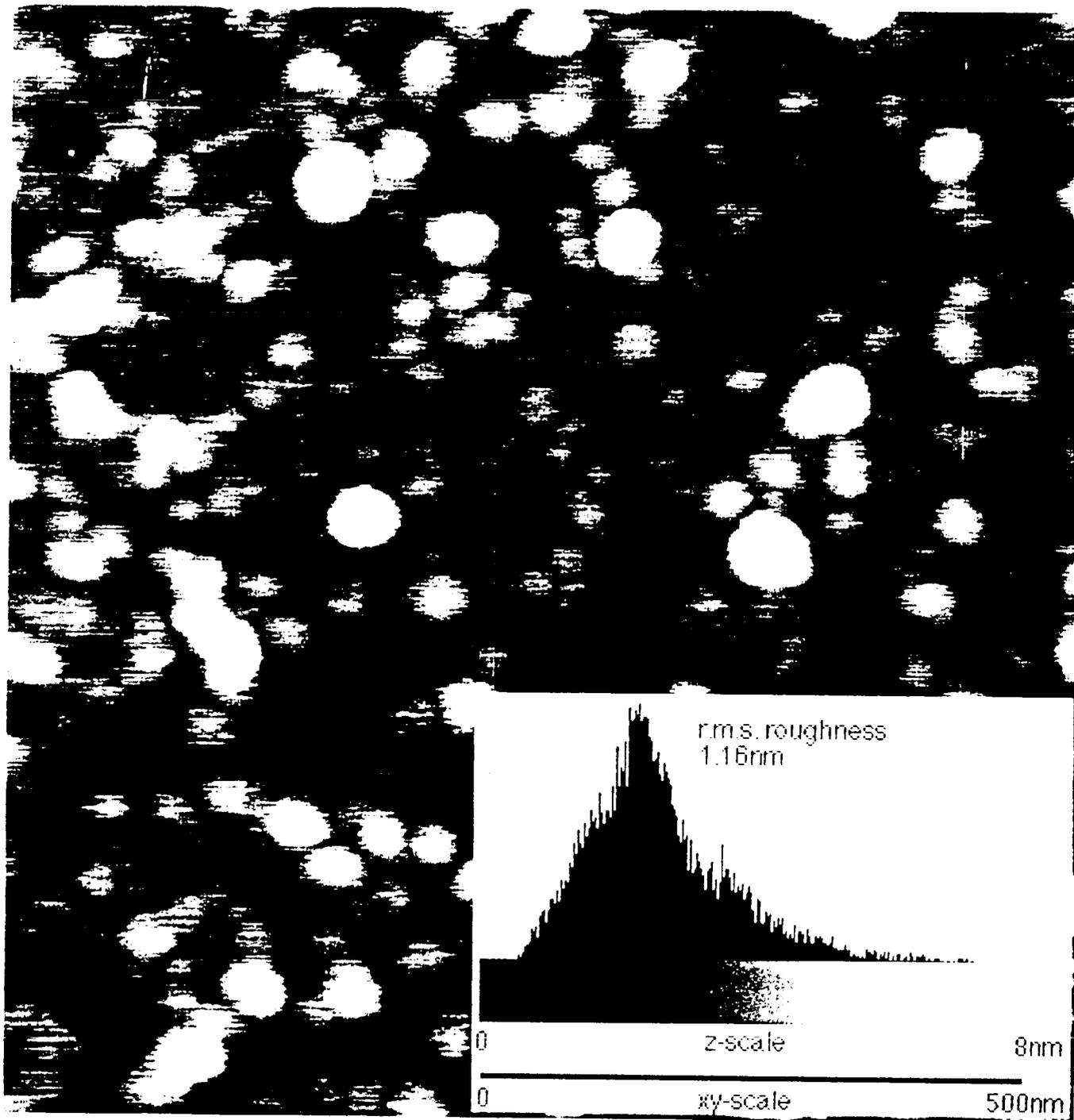


Fig. 7b

Fig 8a





Es: 86
98

Fig 9a and b.

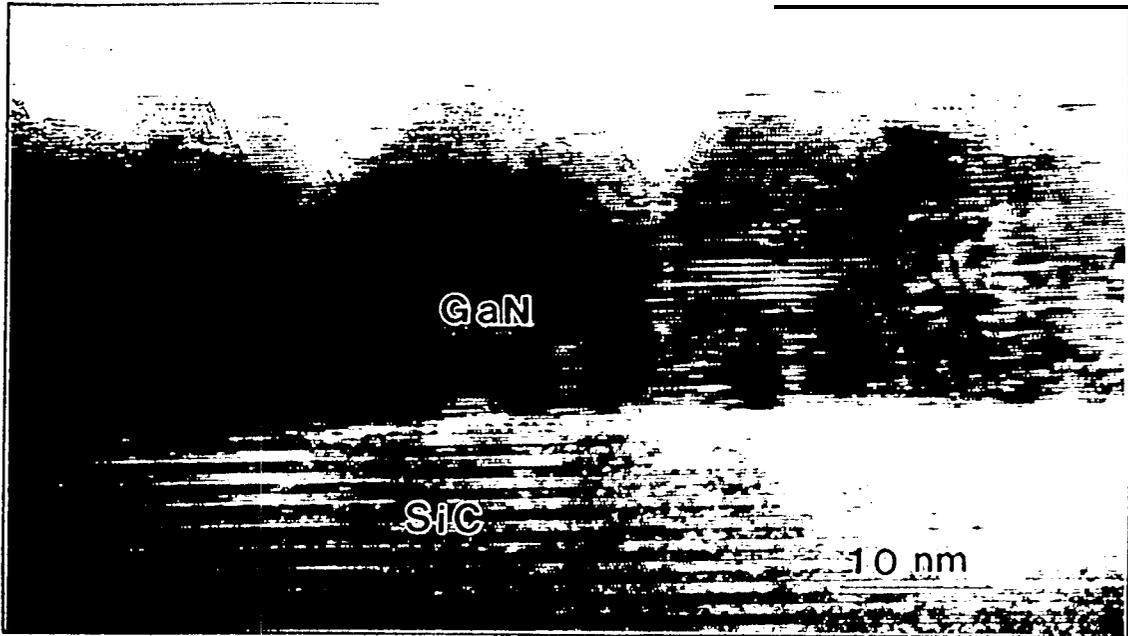


Fig 9a

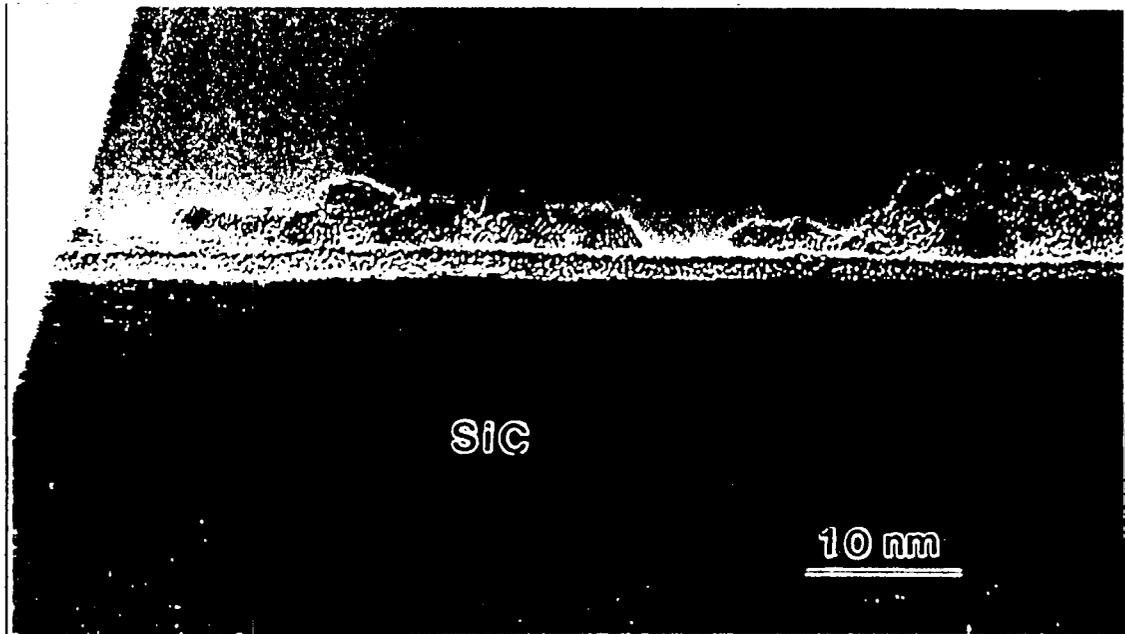
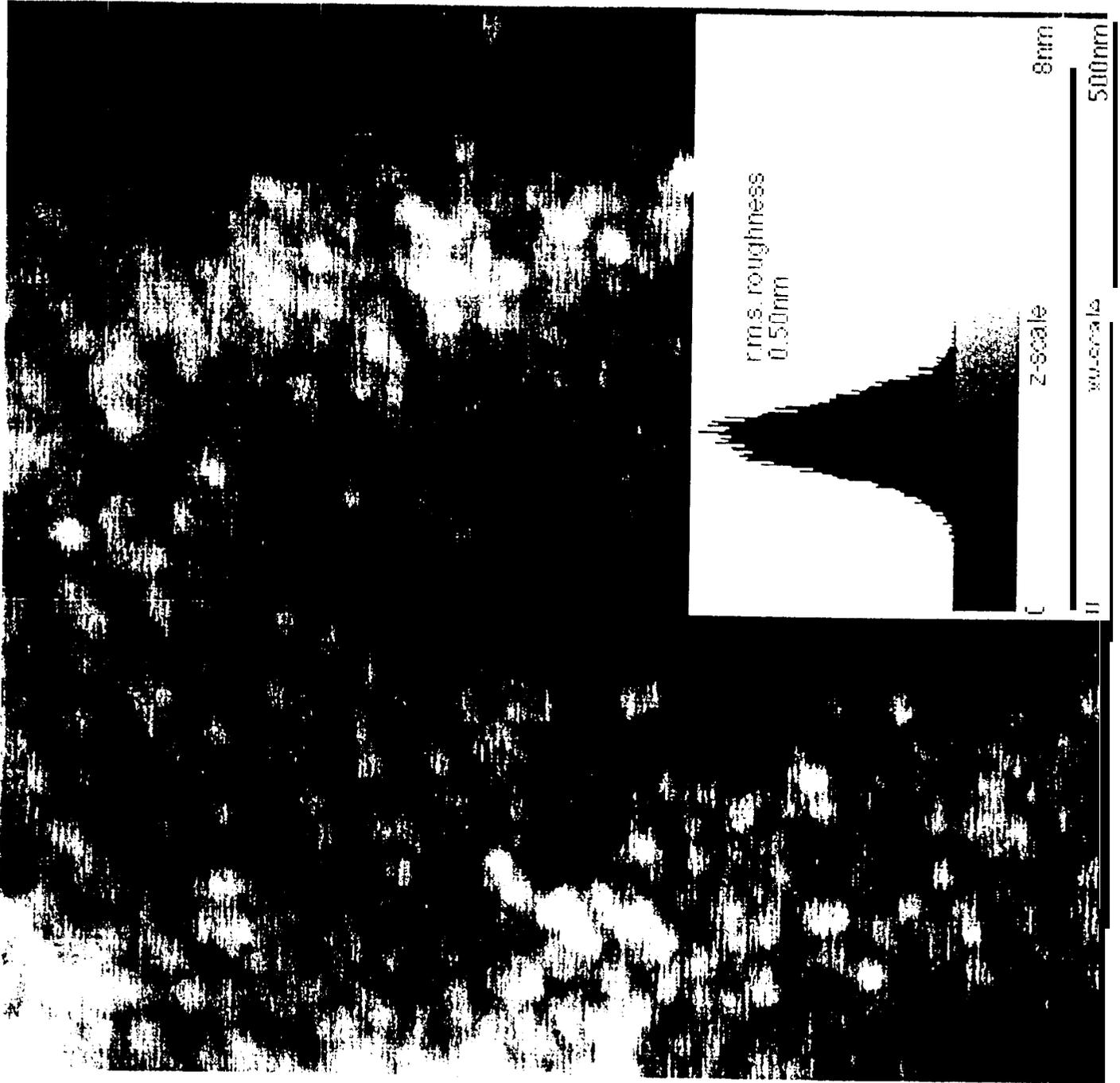


Fig. 9b

Fig. 10a



r.m.s. roughness
0.50nm

8nm

Z-scale

xy-scale

500nm

Kj. 10h

