The miniaturization of integrated circuit devices requires the thickness of the insulating films to be controlled down to the nanometer scale. This makes ultrathin silicon nitride (Si$_3$N$_4$) films interesting, as these may replace SiO$_2$ as a gate dielectric material because of their higher dielectric constant and larger diffusion barrier for dopants. In addition, a higher thermal stability and a larger refractive index make Si$_3$N$_4$ more attractive for e.g. high temperature structural ceramics and anti-reflective coatings, respectively. Moreover, crystalline Si$_3$N$_4$ layers on Si(111) can serve as a substrate for GaN growth to integrate optoelectronic devices to the well-established silicon technology.

Upon deposition of Si$_3$N$_4$ on silicon substrates, the nitride films are usually of amorphous nature. However, thin crystalline Si$_3$N$_4$(0001)/Si(111) overlayers can be formed by thermal nitridation of the Si(111) surface using NH$_3$ [1], NO [2], N$_2$ [3], N-atoms [4] or N-ions [5]. Different results have been reported regarding the structure and the temperature dependence of such Si$_3$N$_4$ films [1–6]. The epitaxial relationship at the interface is favoured by the close lattice match of the Si(111)-2×1 cell (a$_{Si}$=3.84 Å) which is only 1.1% larger than the β-Si$_3$N$_4$(0001) unit cell (7.61 Å) [6].

Although there are some reports on surface reconstructions of Si$_3$N$_4$(0001)/Si(111) overlayers [1, 3], the growth mechanism, surface structural properties and morphological evolution of Si$_3$N$_4$ films depending on nitridation parameters are not yet clear. Within this work, crystalline Si$_3$N$_4$ films were grown by nitridation of Si(111) substrates at elevated temperature using a radio-frequency (rf) N-plasma source. Various growth stages of Si$_3$N$_4$ films starting from the initial stage of nucleation and their morphological evolution in dependence of the growth temperature are discussed.

I. INTRODUCTION

The miniaturization of integrated circuit devices requires the thickness of the insulating films to be controlled down to the nanometer scale. This makes ultrathin silicon nitride (Si$_3$N$_4$) films interesting, as these may replace SiO$_2$ as a gate dielectric material because of their higher dielectric constant and larger diffusion barrier for dopants. In addition, a higher thermal stability and a larger refractive index make Si$_3$N$_4$ more attractive for e.g. high temperature structural ceramics and anti-reflective coatings, respectively. Moreover, crystalline Si$_3$N$_4$ layers on Si(111) can serve as a substrate for GaN growth to integrate optoelectronic devices to the well-established silicon technology.

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II. EXPERIMENTAL

The Si$_3$N$_4$ samples were prepared by exposing the Si(111) surface to an atomic nitrogen flux at an elevated substrate temperature. A radio frequency plasma source (Epi Uni-Bulb) was used as a source of atomic nitrogen. The growth rate of silicon nitride films has been measured to about 0.6 ML/min, which can be used for an estimation of the number of N atoms reacted with the surface Si atoms every minute. The nitridation temperature was varied in a wide range starting from 700°C up to 1050°C. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) were used to characterize the structure and morphology of the nitride films. The preparation and in-situ characterization were performed within an ultra-high vacuum (UHV) chamber having a base pressure of about 5×10$^{-11}$ mbar.

10×2 mm$^2$ pieces from boron doped, highly oriented Si(111) wafers (0.02° miscut along (112) crystalline direction) were used as substrates. After ex-situ cleaning with methanol, the Si(111) samples were thermally degassed at 600°C under UHV conditions. The native oxide was removed by 2–3 short heating cycles at 1200°C for up to 30 seconds. A well-ordered and clean 7×7-reconstructed surface was obtained, as verified by LEED and STM. The sample heating was performed using resistive heating by passing a direct current through it and the temperature was measured by an infrared pyrometer with an absolute uncertainty of about ±30°C. All the STM images presented within this article were recorded in constant current mode.

III. RESULTS AND DISCUSSION

A. Initial nucleation of silicon nitride

To investigate the initial stages of Si$_3$N$_4$ nucleation on Si(111), the surface was exposed to active nitrogen flux for a very short duration. In Fig. 1, the changes of the Si(111) surfaces after rf-plasma exposure for 5 sec at various nitridation temperatures are shown. STM images for both 720°C and 760°C exhibit many small nucleation centers (appearing as dark spots) within the Si(111) terraces as well as larger areas of nucleation at the step edges (appearing also dark) within the upper terrace. Henceforth
FIG. 1: Empty state (-3V, 0.3 nA) STM images of Si(111) surface after exposure to the rf-plasma source for 5 sec at different substrate temperatures as denoted in the labels. Position of the Si(111)-7×7 domain boundaries are indicated by black arrows.

for simplicity these dark dot-like structure will be referred to as 'etch pits'. Comparing the images from 720°C to 760°C, we find that the density of the etch pits is reduced whereas their average size is enlarged. In addition, a careful observation of the STM images shows that the larger etch pits on the terrace are preferentially located along the domain boundaries of the initial Si(111)-7×7 surface (Fig. 1 (b) and (d)). For a further increase of the nitridation temperature to 800°C, this process continues and the density of etch pits is drastically reduced. Moreover, the shape of the nucleation centers becomes much more regular. At the upper side of the step edges, triangularly shaped Si$_3$N$_4$ etch pits have formed. The apex of the triangles is always oriented towards [112], independent of
FIG. 2: Closer view STM image of the 'etch pits' within the Si(111)-7×7 terrace after 5 sec N-plasma exposure at 760°C. The black arrows indicate the initial silicon nitride nucleation in the vicinity of the etch pits. (-2.5 V, 0.3 nA)

The average step orientation in agreement with earlier reports [1]. (The crystalline orientation can be determined by comparing the faulted and unfauluted half of the (7×7) unit cell [7] as well as from the step orientation of the Si(111) surface.) This shape and orientation is also found for most of the etch pits within the terrace. In case of N-atom exposure at 850°C, only a few nucleation centers of even larger size are observed. Inside the etch pits honeycomb-like ("8×8") structures [1, 2] of Si₃N₄ can be observed, as shown in Fig. 1 (h). Details of this structure are discussed later.

An atomically resolved STM image of the Si(111) surface after nitridation at 760°C for 5 sec exposure is shown in Fig. 2. The Si(111) surface appears with etch pits of arbitrary shape. Surprisingly, a clean Si(111)-7×7 reconstruction is found within the pits. The Si(111)-7×7 structures within the etch pits follow the same rotational symmetry as the surrounding Si(111)-7×7 terrace. From this finding, we can conclude that the initial N exposure leads to the surface etching, which results in the evolution of vacancy islands by local removal of the top Si layer. This is accompanied by the formation of silicon nitride, preferentially in the vicinity of the vacancy islands as indicated by black arrows within Fig. 2. A similar kind of observation is also found for plasma treatment at 720°C (image is not shown).

In case of nitridation at 800°C the overall shape of the etch pits becomes regular as shown in Fig. 3. Both images show etch pits of equilateral triangular shape. Inside the etch pits a Si(111)-7×7 surface structure is found for both, filled state (Fig. 3(a)) as well as empty state (Fig. 3(b)) STM imaging condition. Si and/or N adatoms are preferentially found at the periphery of the 7×7 etch pits appearing as bright dots in the STM images. Sometimes, usually for the larger etch pits, adatoms can also be found inside the 7×7 nucleation pits. Distinctly from the etch pits on the terrace, etch pits at the step edges generally show a nitrified Si(111) surface appearing as a disordered structure in the STM images. In Fig. 3(b) a transition from a Si(111)-7×7 structure to a disordered "8×8"-Si₃N₄ structure within the same etch pit is visible. An atomically resolved Si(111)-7×7 structure is observed at the inner side of the etch pit towards the terrace whereas a Si₃N₄ is observed towards the step edge. After nitridation at 850°C, Si(111)-7×7 pits can not be found any more. Instead, only "8×8"-Si₃N₄ structures are observed within both type of nucleation centers.

The decrease in number and increase in size of nucleation centers with increasing nitridation temperature can be explained in terms of thermal diffusion length. For higher substrate temperature, the thermal diffusion is enhanced which causes the reduced number with enlarge size. Furthermore, the larger surface mobility at higher nitridation temperature also influence the shape of the etch pits in favour of equilateral triangles according to the three-fold crystal symmetry of Si(111)-7×7. In summary, only at low nitridation temperature below 720°C, homogeneous nucleation of the silicon nitride pits can be found. At intermediate temperatures, between 760°C and 800°C, heterogeneous nucleation at defects, i.e. at do-
FIG. 4: STM images (-3 V, 0.3 nA) of the structure and evolution of Si(111) surface morphology after nitridation at 800°C for 30 sec and subsequent post-annealing for 1 min at 850°C and 900°C, respectively. Some of the free standing nitride islands are indicated by the black arrows in Figs. (c), (d) and (e).

main boundaries of the Si(111)-7×7 surface and its surface steps govern nucleation. At even higher nitridation temperature, the nucleation of Si₃N₄ occurs at surface steps exclusively. This can easily be understood since the 7×7 structure is not present on the surface due to the 7×7→1×1 phase transition occurring at 830°C [8].

B. Effect of annealing

In Fig. 4, STM images show the Si(111) surface after nitridation at 800°C for 30 seconds ((a) and (b)) and subsequent post-annealing for one minute at 850°C ((c) and (d)) and 900°C ((e) and (f)), respectively. Similar to the observations represented above, after prolonged nitridation at 800°C for 30 sec, many etch pits are formed (Fig. 4 (a)). But the size and density of the triangular nucleation pits are distinctly enhanced with respect to the above-mentioned observation for 5 sec N-atom irradiation. The etch pits partially show a disordered Si₃N₄ structure. These areas appear at a darker contrast within the pits as shown in Fig. 4 (b). After post-annealing at 850°C for 1 min, the structure and surface morphology is significantly changed as shown in Figs. 4 (c) and (d). Etch pits, which were partially filled with disordered Si₃N₄ structures are now completely covered with Si₃N₄ showing an ordered honeycomb-like 8×8 atomic arrangement. Si(111)-7×7 structures are not found anymore within the etch pits. Apart from the structural properties, the size and shape of the nitride nucleation centers have also been altered.
The most prominent changes are found for the nitride pits in close vicinity to the step edges. Some of them have been detached from the upper terrace and form free standing nitride islands on the lower terrace (indicated by black arrows). By comparing with initial image (Fig. 4 (a)) a local retraction of the surface steps towards the upper terrace is observed which results in the formation of free standing islands on the lower terrace now. From a comparison with the corresponding image before annealing, we conclude that a removal of material from the step edge (inverse step-flow growth) is the reason behind this finding. The average size of the free standing islands is larger compare to that of the initial etch pits. The triangular shape of the nitride area has also changed for the free standing island and has turned toward a rather hexagonal shape. Such truncated equilateral triangles can be seen in the STM images of Figs. 4 (c) and (d). The honeycomb-like "8×8" structure is also found within the free-standing nitride islands. In case of further annealing to 900°C for one minute the changes of surface morphology are advancing as shown in Figs. 4 (e) and (f). The average size of the nitride pits and the free standing islands is increased and the movement of the steps is also enhanced which leads to the formation of a broken terrace structure. After annealing at 900°C also an improvement of the quality of the "8×8"-Si₃N₄ structure is found. The formation of a network of nucleation centers (bright dots within the terrace in Fig. (f), see white arrows) connecting the "etch pits" can be attributed to nucleation during cooling of the samples after annealing. During the 7×7 to 1×1 phase transition, domain boundaries form, which offer new nucleation cites for mobile nitride adspecies.

In summary, the changes in surface morphology and structural quality on post-annealing effect can also be explained in terms of temperature induced surface adatom mobility. The high temperature annealing offers better surface mobility of Si atoms and hence better supply of adatom species required for the formation of crystalline Si₃N₄ surface areas. This effect results in the improvement of the structural quality of the Si₃N₄. The removal of upper terrace material is related to the demand of Si atoms to continue the further nitride formation. Initially some of the etch pits were partially covered with Si₃N₄ which later completely transformed into nitride etch pits. The increased size of the nitrided nucleation centers (islands and pits) as well as additional nitride nucleation at 7×7 domain boundaries after high temperature annealing can principally be explained in following way: (a) further nitridation from residual gas (b) reaction with surface N-adatoms and (c) Ostwald ripening. As residual gas contains only molecular nitrogen, the first concept is most unlikely for further nitridation process at this temperature. Local regrowth by surface N-adatoms is possible as they become mobile during annealing. However, the decrease in the density of nitride pits during annealing-induced enlargement suggests that Ostwald ripening is most likely the key process behind it. The change in the shape of free standing island from triangular to truncated-triangular / distorted-hexagonal shape can be related to the hexagonal symmetry of the Si₃N₄ crystal. However, the shape of the nitride etch pits inside the terrace areas is still triangular which is in agreement with the three fold crystal symmetry of Si(111). The nucleation around the domain boundary can also be explained in terms of defect induced nucleation as discussed earlier for surface steps.

C. Surface reconstruction of β-Si₃N₄

After nitridation of Si(111) at sufficiently high substrate temperatures (above 800°C) a honeycomb-like atomic arrangement of Si₃N₄ surface is obtained for thinner nitride films (coverage < 2 ML). This structure has an average surface periodicity of about eight times the Si(111) lattice distance, i.e. 30.6Å. Within this article, this type of nitride surface structure is mentioned as honeycomb-like "8×8"-reconstruction of β-Si₃N₄. For nitridation temperatures below 800°C, the honeycomb-like structures are found but show a high defect density and poor crystal order. High temperature nitridation and post-nitridation annealing however, improves the structural order signifi-
FIG. 6: LEED pattern of "8×8"-reconstructed β-Si₃N₄ surface grown at 900°C. Diffraction spots correspond to the Si(111) and Si₃N₄ lattice are mentioned within the LEED image.

significantly. Empty state STM images of the honeycomb-like "8×8" surface are shown in Fig. 5. Here, the nitridation was performed at 850°C for 30 sec. A defective quasi-periodic network with local disordering can be observed in Fig. 5(a). At a closer inspection of the honeycomb-like surface area, atomically resolved structures are found as depicted in Fig. 5(b). An autocorrelation mapping of the honeycomb-like structure (inset of 5(b)) also confirms a surface periodicity of about 30.6 Å, indicating an "8×8" surface reconstruction of Si₃N₄ structure which is rapidly obtained in LEED imaging as shown in Fig. 6.

The appearance of honeycomb-like "8×8" atomic structures of the β-Si₃N₄(0001) surface with local disordering can be explained in the following way. As it is only observed for very thin films (Si₃N₄ coverage below 2ML), the structures observed in STM may be related to states of the Si₃N₄-Si(111) interface which has a highly distorted bonding configuration due to the substrate-epilayer lattice mismatch.

IV. CONCLUSION

In summary, the formation of thin silicon nitride films producing by a rf plasma-assisted nitridation and various stages of the initial nucleation process have been investigated by scanning tunneling microscopy. It has been found that the initial Si₃N₄ nucleation always occurs at the upper terrace at the step edges of Si(111) or within terrace areas by forming nucleation pits. Low temperature nitridation (up to 720°C) results in a homogeneous nucleation of the nitride pits whereas for higher nitridation temperatures (760–800°C), defect induced heterogeneous nucleation at domain boundaries of the Si(111)-7×7 surface and its surface steps dominates. Lower nitridation temperatures results in nitride films of poor crystalline quality whereas high temperature nitridation or annealing leads to the formation of a crystalline β-Si₃N₄ films with "8×8" surface reconstruction for ultra-thin films, which has been atomically resolved with STM.

Acknowledgments

We would like to thank Wacker Siltronic AG, Burghausen for providing high-precision oriented Si(111) wafers.