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In situ DC-plasma cleaning of silicon surfaces

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Abstract

The native oxide and carbon contamination on silicon wafers are removed in situ by a direct current H/Ar-plasma cleaning process. The residual contamination after the surface cleaning lies under the detection limit of secondary ion mass spectroscopy (SIMS). However, scanning tunneling microscope (STM) measurements show a surface roughness with a peak-to-peak amplitude of 4 nm on a lateral scale of 20 nm. Photoemission results (UPS) reveal the dangling bonds to be saturated with hydrogen. Upon annealing, reflection high energy electron diffraction (RHEED) and thermal desorption spectroscopy (TDS) show that the surfaces flatten after the final hydrogen desorption step at temperatures of 450–500°C.

1. Introduction

The trends in modern silicon-based microelectronics are pointing in the direction of in situ processing at low temperatures to achieve sharp doping profiles and to make use of heterostructures composed of ultra-thin films. In this context in situ cleaning at low substrate temperatures is one of the most important processing steps. Different hydrogen-plasma etching facilities, using ECR or RF plasmas [1–4], have been developed to reach this goal. Recently, Ramm et al. [5,6] showed that a low energy (discharge voltages smaller than 30 V) DC plasma process, called plasma chemical cleaning, can be used to clean silicon surfaces from the native oxide and carbon contamination without any pretreatment of the wafers. Since all atomic species forming volatile compounds with hydrogen are removed in the plasma process, the silicon itself can also be etched. Typical etching rates of the DC plasma process are 1 nm/min for Si and SiO_x and 5 nm/min for diamond-like carbon. Plasma-cleaned Si(111) and Si(100) surfaces are well suited for subsequent homoepitaxial overgrowth [7], although hydrogen incorporation during the plasma exposure leads to strain in the substrate of up to 0.3% [8].

In this article we characterize Si(100) and Si(111) surfaces after the cleaning process and after additional annealing steps by means of scanning tunneling microscopy (STM), X-ray and ultra-violet photoelectron spectroscopy (XPS, UPS) and reflection high energy electron diffraction (RHEED). Quantitative SIMS (secondary ion mass spectroscopy) profiles taken on a silicon-capped sample are used to determine the residual contamination after the cleaning step. The hydrogen desorption upon annealing is additionally investigated by thermal desorption spectroscopy (TDS).

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2. Experimental

The UHV plasma chemical cleaning module based on the Balzers ULS 400 is connected to the existing VG-MBE (molecular beam epitaxy) unit equipped with different surface analysis tools such as UPS, XPS and RHEED. A chamber with a home-built STM is also attached to the MBE unit [9]. The base pressure in these analysis chambers is better than 10^{-10} mbar whereas the base pressure in the cleaning chamber lies around 10^{-9} mbar due to the hydrogen memory effects of the chamber walls.

The plasma is generated by the plasma source (Fig. 1) consisting of a separated cavity with a heated Ta filament. When argon is fed into the cavity and a potential of 20–30 V is applied between the filament (cathode) and ground (anode), a high electron current discharge is initiated between the filament and the chamber walls of the cleaning module. The electrons of the discharge activate additional reactive gases (here hydrogen) forming different excited species and ions such as H_3^+, ArH^+ and H_2^+ [6].

In these experiments, the substrate was left floating, resulting in a negative potential of about 10 V with respect to the plasma. This gives an upper limit to the ion energies involved. Thus, any surface damage stemming from the ion bombardment should be small. During the cleaning, the pressure in the chamber amounts to $(5–10) \times 10^{-3}$ mbar.

Structured epitaxial $CoSi_2$ layers (3 nm thickness) are used to determine the etching rate of silicon. $CoSi_2$ is not detectably etched by the plasma process since cobalt does not form a volatile compound with hydrogen and hence can be used as an etching mask. On $CoSi_2$ films patterned by ex situ selective wet chemical etching, the 3 nm thick silicide is still present even after 4 h of plasma cleaning, whereas 240 nm of the bare silicon are removed, as measured using optical interference microscopy. (The results of cleaning $CoSi_2$ by the same plasma process will be discussed in a forthcoming paper.) The etching rate of silicon amounts thus to 1.5 nm/min for these particular plasma conditions and is homogeneous over the whole wafer surface.

As-received (111)- and (001)-oriented silicon wafers (3 inch diameter) are introduced into the system without precleaning and outgassed at 500–550°C for 30 min. Then the wafers are transferred to the plasma chamber and cleaned by the plasma process for 10 min. During the plasma exposure the sample temperature rises to the range of 150–200°C. This temperature was measured in a separate experiment by attaching a thermocouple in front of a test wafer. For further analysis the samples are transferred to the MBE system.

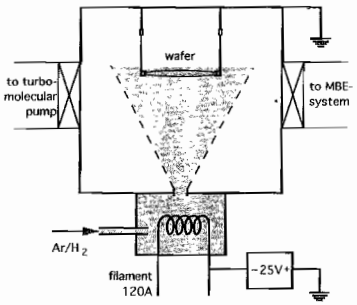

Fig. 1. Schematic view of the plasma-cleaning module.

3. Results and discussion

3.1. Cleaning of Si(111) and (001)

After the plasma cleaning process (10 min) the native oxide is removed and the carbon surface contamination is below the detection limit of XPS (0.1 monolayer). No interface carbon contamination on a sample capped with silicon at room temperature (RT) could be detected by means of quantitative SIMS, which gives a more accurate quantification of the residual contaminants (detection limit: 10^{-3} monolayer).

In RHEED diagrams, strong three-dimensional reflections and a significant diffuse background are visible after the plasma cleaning, indicating the formation of a disordered and rough surface. A surface roughness is found in STM topographs, indeed, as shown in Fig. 2a. The cross section (Fig. 2b) reveals a peak-to-peak amplitude of typically 4 nm on a lateral scale of 20–30 nm. Atomic resolution could not be obtained because of the surface roughness.

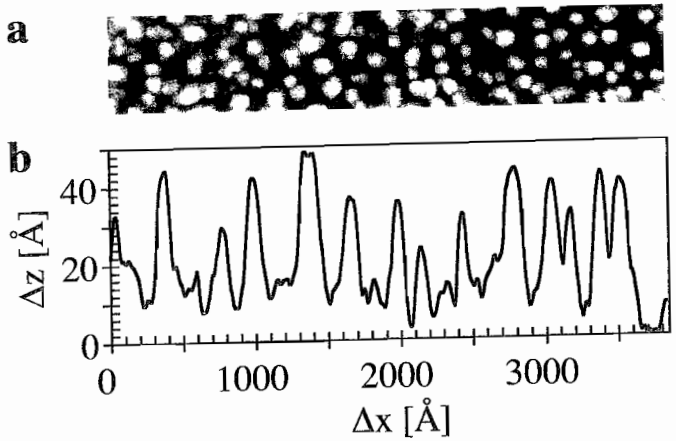

Fig. 2. (a) STM topograph after the plasma cleaning of a Si(111) surface (tip bias $V_t = 3$ V, tunneling current $I_t = 0.5$ nA). (b) Corresponding cross section showing the surface roughness (note the expanded scale in z-direction).

Nevertheless, the appearance of three-dimensional spots in the RHEED patterns is a strong sign that the protrusions seen with the STM exhibit crystalline order and that surface damage in the plasma process is limited to the very surface, if it occurs at all.

Figs. 3 and 4 present the UPS results of Si(001) and Si(111) taken with He I excitation, respectively. For both orientations, two main differences can be observed between the plasma cleaned surfaces (spectra on top) and the bare silicon surfaces obtained by growing buffer layers by MBE (spectra at bottom). First, one notices an enhanced intensity in the 4–8 eV binding energy region. In particular, the minimum in the bulk valence band density of states (DOS) around the binding energy of 5.5 eV is filled up. Secondly, no sign of the usual surface states of the 2×1 or 7×7 reconstruction are detected in the gap region. Instead, a smooth onset of the valence band can be seen [10]. In more detail, a peak at a binding energy of about 6 eV arises after the plasma cleaning of the Si(001) surface. It is not well resolved and seems to be accompanied by a broader background, adding photoemission intensity to the bulk derived features on both sides. The characteristic of the plasma-cleaned Si(111) surface at RT is a strong intensity enhancement and a broadening of the bulk feature at 7.4 eV together with a weak shoulder at 6.0 eV binding energy.

Hydrogen chemisorbed at Si(001) and Si(111)

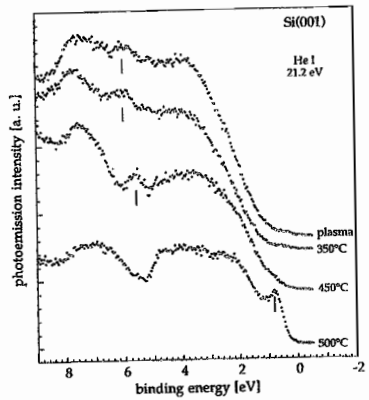

Fig. 3. Angle-integrated ultra-violet photoemission spectra (UPS) taken with He I radiation of the plasma-cleaned Si(001) surface and after different annealing steps. The spectrum labeled 500°C is identical to the spectrum of the Si(001)2×1 surface obtained by growing a buffer layer by MBE at 700°C.

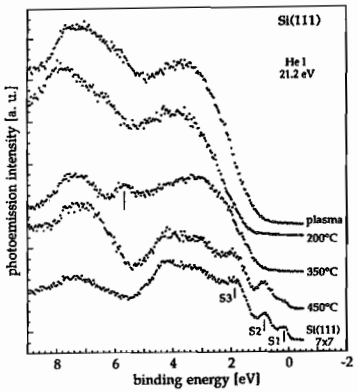

Fig. 4. Angle-integrated ultra-violet photoemission spectra (UPS) taken with He I radiation of the plasma-cleaned Si(111) surface and after different annealing steps. At the bottom, the spectrum of the Si(111)7×7 surface obtained by growing a buffer layer by MBE at 700°C.

surfaces has been studied extensively in the past. Exposures to atomic hydrogen at RT lead first to the formation of Si–H (monohydride) species and, at higher doses, to Si–H_2 (dihydride) [11–14]. Trihydride is also found, particularly on Si(111) [15]. On the Si(001) surface the monohydride gives rise to a well resolved peak at 5.6–6.0 eV binding energy in UPS [2,14], whose energy seems to depend on the exact preparation condition of this phase [10] as well as on the spectrometer geometry. The dihydride phase on this surface adds photoemission intensity centred at about the same energy as the monohydride phase but spread over a larger energy range (roughly from 4 to 8 eV). The prominent dangling bond surface state at 1 eV is not found on hydrogenated surfaces. The monohydride Si(111) surface is characterized in UPS by two peaks at 5.3 and 7.4 eV binding energy [12]. At RT, the di- and probably the trihydrides give an additional feature at 6.2 eV together with a wider spread intensity enhancement. Therefore, the formation of the different hydrides at the surface intensifies the emission around the structure at 7.4 eV binding energy and fills up the minimum of the valence band DOS at 5.5 eV. A combination of the different hydrides should result in an enhanced photoemission intensity between 5 and 8 eV binding energy, compared to the clean surface. In LEED, surfaces highly saturated with hydrogen exhibit no 7×7 surface reconstruction [16]. Accordingly, the three well known surface states at 0.7 (S2) and 1.8 eV (S3) binding energy and near the Fermi level (S1), assigned to dangling bond (S1, S2) and back-bonding (S3) states of this reconstruction, are absent in UPS [12].

The comparison of our photoemission spectra to these results is complicated by the fact that no well defined orientation is present because of the surface roughness. Nevertheless, the enhanced intensity in the minimum of the valence band DOS together with the absence of any structure above the valence band maximum (where on the clean surfaces the dangling bond derived states can be found) are common to both orientations and are clearly visible in our spectra. This leads us to conclude that DC plasma cleaned silicon surfaces at RT are strongly hydrogenated, and that all dangling bonds are saturated with hydrogen. The main species present at the surface is silicon dihydride, though the monohydride seems also to exist. One may speculate that silicon trihydride is also likely to be formed since the rough surface may contain a considerable number of singly bound adatom trihydrides.

3.2. Low-temperature annealing

Upon annealing of the Si(001) surface, hydrogen desorption increases slowly up to temperatures around 350°C (see dots in Fig. 5). At higher temperatures two hydrogen desorption maxima are detected around 400 and 460°C, the latter being more intense. The RHEED pattern shows a slight reduction of the background intensity at lower temperatures, but only at the second hydrogen desorption maximum, at 460°C, do the three-dimensional spots disappear and the pattern of the 2×1 reconstruction becomes visible. In UPS, the peak around 6 eV binding energy becomes more intense upon annealing at low temperatures of 200–350°C (Fig. 3). During the first hydrogen desorption maximum, photoemission intensity is lost at the minimum of the valence band DOS around 5.5 eV while the fine peak, now at 5.6 eV [10], still persists. Just below the Fermi level, a slightly enhanced intensity may be interpreted as the first trace

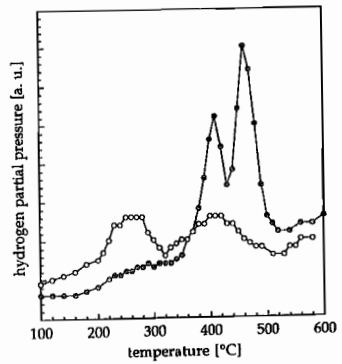

Fig. 5. H_2 partial pressure as a function of temperature of the plasma-cleaned Si(001) (●) and Si(111) (○) surfaces measured by means of a quadrupole mass spectrometer. The annealing rate is 50°C/min.

of the appearing surface state. After the second hydrogen desorption maximum, the UPS spectrum can hardly be distinguished from that of the clean Si(001)2×1 surface. In particular, the surface state at 0.8 eV binding energy can now clearly be seen.

On the (001) surface, these observations are quite consistent with earlier desorption experiments on hydrogenated silicon [13–15,17]. A first hydrogen desorption maximum was found at 360–410°C and attributed to the transition from the di- to the monohydride surface phase which in LEED is accompanied by a change from a 1×1 to a 2×1 pattern [14]. We were not able to detect this transition in RHEED, because the surface pattern was masked by the three-dimensional spots. As already pointed out, the dihydride shows a higher photoemission intensity in the 4 to 8 eV binding energy region than the monohydride. Hence the observed reduction in this spectral range between the samples annealed at 350°C and 450°C, respectively, gives evidence of the transition to the monohydride phase during the first hydrogen desorption step. The second desorption peak usually found at 480–530°C, stems from hydrogen in the monohydride phase [13], resulting in the clean 2×1 reconstructed Si(001) surface, which in UPS is characterized by the prominent surface state at 0.8 eV binding energy. This last development upon annealing is reproduced in our experimental findings, although at a lower temperature than expected (460°C instead of about 520°C), which might stem from the high step density of the rough surface.

Annealing of the plasma cleaned (111) surface results in two broad and weak maxima in the hydrogen desorption at 200–300°C and at 420–450°C, respectively (see circles in Fig. 5). During the first desorption stage, the intense photoemission feature at 5–8 eV binding energy is split into two peaks at 5.7 and 7.4 eV binding energy at (Fig. 4). In RHEED the three-dimensional spots visible right after the plasma clean persist up to the second hydrogen desorption at 420–450°C. At higher temperatures a 1×1 pattern becomes visible, accompanied by the gradually appearing 7×7 reflections from 480°C on. In UPS the characteristic surface peaks of the reconstructed Si(111) surface can be seen already at an annealing temperature of 450°C, though the S1 state at the Fermi energy, attributed to the dangling bonds of the adatoms [18], has only a weak intensity. The hydrogen induced state at 5.7 eV has disappeared, but the spectral weight of the peak at 7.5 eV binding energy is still enhanced.

In the literature, hydrogen desorption from the saturated Si(111) surface is known to occur in two steps [11,16] corresponding to the β_2 (410°C) and β_1 (540°C) desorption peaks. The β_2 maximum is supposed to be due to the decomposition of di- and trihydrides, while the β_1 peaks reflects the desorption from the monohydride phase. In our TDS observations, however, no hydrogen desorption peak could be detected above 500°C. The important discrepancies between our observations and what is expected from the desorption of the Si(111) surface are probably related to the surface morphology after the plasma cleaning. The initial surface roughness, probably composed of facets with different orientation, together with a large number of steps may cause the desorption peaks to smear out. The absence of the β_1 desorption above 500°C may be a hint that the monohydride Si(111) surface is not likely to form and that the facets have probably {001} or {110} orientations.

It is interesting to note that on both, the Si(001) and the Si(111), surfaces the final hydrogen desorbs

t nearly the same temperature (~ 450°C), where, at ıe same time, the three-dimensional spots in RHEED isappear and the surface reconstructions are built ɔ. This shows that the surface roughness can be rongly reduced upon annealing the surfaces at tem-ɛratures around 500°C. Furthermore, the removal of ıe hydrogen from the surface seems to be critical to ıhance the surface mobility necessary for flattening.

Conclusion

The cleaning of silicon wafers near RT was hieved by means of an argon–hydrogen DC plasma ocess. We emphasize the fact that no pretreatment the wafers was necessary to achieve residual rbon contamination below the detection limit of MS. The surface dangling bonds are saturated by drogen, which reduces drastically the re-oxidation wafers exposed to the ambient as observed in ?S. The surface morphology, however, is not ideal, owing roughness of 4 nm on a lateral scale of –30 nm. On the Si(111) surface, this plasma-in-ced surface roughness affects the thermal desorp-n of hydrogen in an important way. Nevertheless, : desorption of the hydrogen at temperatures below 0°C enhances the surface mobility, resulting in tter surfaces exhibiting the usual 2×1 or 7×7 :onstruction of Si(001) or Si(111), respectively.

knowledgments

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References

[1] M. Delfino, S. Salimian, D. Hodul, A. Ellingboe and W. Tsai, J. Appl. Phys. 71 (1992) 1001.
[2] M. Diani, J.L. Bischoff, L. Kubler and D. Bolmont, Appl. Surf. Sci. 62 (1992) 67.
[3] B. Anthony, L. Breaux, T. Hsu, S. Banerjee and A. Tasch, J. Vac. Sci. Technol. B 7 (1989) 621.
[4] J. Cho and R.J. Nemanich, Phys. Rev. B 46 (1992) 15 212.
[5] J. Ramm, E. Beck and A. Zueger, Mater. Res. Soc. Symp. Proc. 220 (1991) 15.
[6] J. Ramm, E. Beck, A. Dommann, I. Eisele and D. Krüger, Thin Solid Films 246 (1994) 158.
[7] J. Ramm, E. Beck, A. Züger, A. Dommann and R.E. Pixley, Thin Solid Films 222 (1992) 126.
[8] J. Ramm, E. Beck, A. Züger, A. Dommann and R.E. Pixley, Thin Solid Films 228 (1993) 23.
[9] H. Sirringhaus, E.Y. Lee and H. von Känel, J. Vac. Sci. Technol. B 12 (1994) 2629.
[10] The onset of the valence band depends strongly on the hydrogenation state. This is partially due to the suppressed band bending on hydrogenated sufaces. Not only the valence-band maximum, but all the features of the valence band (and the core levels) are shifted by the same amount of energy.
[11] B.G. Koehler, C.H. Mak, D.A. Arthur, P.A. Coon and S.M. George, J. Chem. Phys. 89 (1988) 1709.
[12] J.J. Koulmann, F. Ringeisen, M. Alaoui and D. Bolmont, Phys. Rev. B 41 (1990) 3878.
[13] Y.M. Wu and R.M. Nix, Surf. Sci. 306 (1994) 59.
[14] C.C. Cheng and J.T. Yates, Jr., Phys. Rev. B 43 (1991) 4041.
[15] J.J. Boland, J. Vac. Sci. Technol. B 9 (1991) 764.
[16] G. Schulze and M. Henzler, Surf. Sci. 124 (1983) 336.
[17] L.S.O. Johansson, R.I.G. Uhrberg and G.V. Hansson, Phys. Rev. B 38 (1988) 13 490.
[18] F.J. Himpsel, B.S. Meyerson, F.R. McFeely, J.F. Horar, A. Taleb-Ibrahimi and J.A. Yarmoff, in: Proc. Int. School of Physics "Enrico Fermi" (Varenna 1988), Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation (North-Holland, Amsterdam, 1990).

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Charge transfer processes in a-WO_3/Si heterostructure during electro- and photochromism

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Abstract

Heterostructure a-WO_3/Si was obtained by vacuum condensation of thermally evaporated tungsten trioxide powder on n-Si substrate under conditions leading to formation of a transparent WO_3 film (stoichiometric) and with color centers (partially reduced). For both types of structures, high frequency C–V characteristics have been investigated as well as an influence of color center formation in a-WO_3 on charge parameters of heterojunction at the double injection of protons and electrons into the film and with UV irradiation for different exposure times. A single energy level of fast surface states was found in the structure with WO_{3-x} film arranged by 0.06 eV below the Fermi level in Si. Density of states at this level increases in electrochromic process and decreases in photochromic one. A structural-energy model of coloring process is proposed.

1. Introduction

Perovskite-like oxide materials exhibit a wide range of interesting properties. Specific features of the atomic and electronic structure of these compounds, which determine the variety of observed phenomena and which have not been studied in detail yet, result in a strong dependence of the properties (local order, optical absorption, conductivity) on exposure to external factors (ambient conditions, irradiation, electron and ion injection, reduction–oxidation). These dependences appear as electro- and photochromic effects.

Being of great interest, these effects are most prominent in thin films of amorphous tungsten trioxide (a-WO_3). This material therefore is the main object of applied and fundamental investigations of the mentioned phenomena (electro- and photochromism) and the most promising material for an all-solid-state design of passive displays [1].

Note, that the process of reversible coloration in a-WO_3 has a rather complex character. Moreover, the considered object is not in thermodynamical equilibrium. Apart from that, the physics of disordered materials is hardly developed. These reasons cause the fact that only a general pattern of coloration has been reliably established up to now. For specific features of electro-, photo- and thermochromism, only scattering data are available which does not allow one to design a comprehensive picture even at a phenomenological level. The conventional concept on the structural and energetical model of color centers in a-WO_3 is also absent.

An electrochromic display is a charge device and the electrons injected into a-WO_3 thin film during coloration are localized on the levels in the energy

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