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INFLUENCE OF OXIDATION PARAMETERS ON ROUGHNESS AT THE SI-SIGER I---ETC(U)

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6-80

DA-ER0-70-6-011
Influence of Oxidation Parameters on Roughness at the Si-SiO₂ Interface.

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The roughness at the interface Si-SiO₂ has been determined on an atomic scale after removal of the oxide by LEED (Low Energy Electron Diffraction). The energy dependent broadening of the diffracted electron beams yields the average size of step free terraces. Silicon (111) samples have been oxidized under various conditions concerning atmosphere (dry and wet oxygen), temperature (800°C and 1000°C), time, intertreatment and posttreatment. The oxidation process produces a roughness which may be decreased by low oxidation rates.

Silicon Surface
Si-SiO₂ Interface
LEED (Low Energy Electron Diffraction)
Roughness Determination
Influence of Oxidation Parameters on Roughness at the Si-SiO₂ Interface

Final Technical Report

by

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January 80

EUROPEAN RESEARCH OFFICE
United States Army
London, England

Grant Number DA-ERO 78-G-011
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Summary

The roughness at the interface Si-SiO$_2$ has been determined on an atomic scale after removal of the oxide by LEED (Low Energy Electron Diffraction). The energy dependant broadening of the diffracted electron beams yields the average size of step free terraces. Silicon (111) samples have been oxidized under various conditions concerning atmosphere (dry and wet oxygen), temperature (800$^\circ$ C and 1000$^\circ$ C), time, pretreatment and posttreatment. The oxidation process produces a roughness, which may be decreased by low oxidation rates and appropriate annealing in non-oxidizing atmosphere. The novel technique of evaluation for the first time shows systematically, how oxidation parameters determine the roughness at the interface, which again is important for the performance of MOS-devices.

Keywords: Si-SiO$_2$ interface
LEED (Low Energy Electron Diffraction)
Roughness determination
Structural properties
Silicon surface
I. Introduction

The quality of MOS-devices depends among other parameters strongly on the quality of the interface between silicon and silicon-dioxide. Whereas the chemical composition (like segregation of alkali ions) and electrical properties (interface states, interface charge, scattering of electrons at the interface) have been studied for a long time, the structural properties had been neglected due to lack of appropriate measuring techniques. Only recently several new techniques have been applied. Depth profiling by ion bombardment and monitoring of the varying chemical composition of the surface during removal of the oxide provides some information on a "transition layer". The assumption, however, is required that the ion beam does not produce a roughness of the same order of magnitude. Transmission electron microscopy of cross sections of MOS structures shows directly the profile of the interface. A quantitative interpretation is still difficult.

A novel technique for studying the interface uses electron diffraction (LEED). If the surface of a single crystal shows different levels due to atomic steps, the diffracted electron beam is modified by interference of the electrons diffracted at adjacent terraces. By varying the energy and therefore also the wave length of the electrons this interference changes periodically between constructive and destructive interference. Therefore the spot shape changes periodically with increasing energy. From the period the step height is derived with high precision (< 1% of step height), from the spot shape the distribution of terraces with respect to orientation, width and regularity is obtained (for details see references 1 - 4).

This method may be applied also to study the interface of Si and SiO₂. After removal of the oxide the roughness of the interface is seen directly due to the broadening of the
diffraction spots, which changes periodically with electron energy. Whereas the Annual Technical Report (March 79) has presented the first systematic results, the present Final Report shows, how the oxidation time, temperature and treatments before and after oxidation influences the roughness at the interface as measured after removal of the oxide. The theoretical aspects of the interpretation of the LEED-pattern have been reviewed and are part of this report (already published in Adv. in Sol. State Physics XIX, p 193, J. Treusch (ed.), Vieweg, Braunschweig 1979).

II. Experimental

For the experiments a UHV-system has been set up with a four-grid-LEED system (Physical Electronics). The LEED spots at the phosphoric screen have been profiled with a closed TV-system (Hamamatsu). A sample transfer system enabled a quick exchange of samples. The details have been described in the Annual Report (March 79). In the meantime two improvements have been added: an automated recording and evaluation of the LEED spot profile and an extension of oxide thickness measurements to very low thickness with the help of Auger Electron Spectroscopy.

a) On-line LEED spot profiling.

The LEED spots at the phosphoric screen have been profiled with a closed TV-system (Hamamatsu). The schematic configuration is seen in fig. 1. The system may be operated with 256 up to 1024 lines per image. One vertical column of spots of the image at an arbitrary horizontal position is digitalized and shown as an intensity profile within the screen of the monitor. By rotation of the camera an arbitrary cross section of a spot may be chosen.
The intensity profile is first recorded by a transient recorder which is able to store 2048 numbers with 8 bit resolution. By use of an on-line computer (PDP 11) the data may be recorded directly by an xy-recorder or processed for any kind of evaluation.

The software (in FORTRAN) enables a wide variety of procedures. In the usual procedure the program first determines the distance of the 00-spot from the 10 spot on the screen, since the half width of the spots has to be calculated relative to this distance (see Annual Report, March 79). For determination of the half width the following data are given to the computer: energy of electrons, number of cycles for accumulation, time of integration for each cycle. The computer provides the optimum voltage for focussing of the electron beam, which (so far) has to be done manually. Then the computer collects and accumulates the intensity profiles, selects a field of 200 points each on both sides of the maximum spot, determines and subtracts the background and calculates the half width relative to the next spot distance. After manual change of the electron energy or sample position the procedure is repeated.

The FORTRAN program and some of the macro subroutines are given in the appendix.

The determination of edge atom densities from relative half width is already given in the Annual Report (march 79) and in the included review paper.

b) Oxide thickness determination for very thin oxides

To extend the measurements of roughness to interfaces at very thin oxide layers, an alternative method to the Tolanski method (see Annual Report, March 79) has been applied which is limited to thickness \( d > 15 \text{ nm} \). With Auger
Electron Spectroscopy the binding energy of silicon atoms may be measured. Since in oxide this binding energy is shifted by a few electron volts (chemical shift), a high resolution electron spectrometer can distinguish between silicon atoms in oxide and in bulk silicon. C.C. Chang and D.M. Boulin (5) have calibrated this method by a determination of the exponential decay of electron escape probability for different distances of the originating silicon atom from the surface. At an energy of 1615 eV they found an escape depth of 3.1 ± 0.9 nm in SiO₂. The method is suited up to oxide thickness of 12 nm.

A commercial cylindrical Auger Electron Spectrometer (Physical Electronics) with an energy resolution of 0.3%, lateral resolution of 5 μm and an coaxial integral gun has been used. The spectra have been recorded with a 2 volt peak-to-peak modulation and an incident electron beam of 5 - 10 μA at 6.6 keV. In fig. 2 it is seen that the clean (a) and heavily oxidized surface (c) show two easily distinguishable recordings. From the intensity ratio at thin oxides (b) the oxide thickness is derived.

III Influence of procedure on the results

a) Cleanliness of samples after removal of oxide

To find out the state of the surface after removal of the oxide, Auger Electron Spectroscopy has been applied to several samples, treated as for the LEED experiments.

The samples checked were oxidized with various oxidizing parameters. One sample was oxidized by Siemens AG, München, within their commercial standards. Some AES spectra are shown in fig. 3. Besides silicon (92 eV) only oxygen
(503 eV) and carbon (272 eV) is found. No other contamination was detectable. The peak-to-peak signals are representative for the surface concentrations of the respective elements. The ratio of the signals of Si to C and O was about 100:5:5 for the commercial sample and nearly identical (100:7:7) for the own samples. According to the calibrations as reported by Kasupke (6) and Klimesch (7) the coverage of carbon and oxygen is about 0.3. It is obvious that the surface is not clean on an atomic scale. On the other hand this amount of contamination just can produce some background of the LEED pattern, it, however, can not influence the oscillation of the half width of the LEED spots. Therefore the conclusion is supported, that the observed oscillations are due to the step structure of the silicon itself.

After many cycles of sample exchange the sample holder (which is a single crystal of silicon itself) showed a much higher carbon and oxygen coverage, although it had been etched each time in HF together with the samples. Therefore the sample holder was contaminated with hydrocarbons and other compounds (containing hydrogen, carbon and oxygen), which were not removed by etching (see fig. 3.b). This contamination increased the background in the LEED pattern and deteriorated the LEED spots. Oxidizing the holder and etching together with the samples restored a bright LEED pattern.

b) Influence of treating in nitrogen, air and methanol

Since the samples between etching in HF and observing in UHV have to handled in liquids and atmospheres, it is necessary to check, if those parts of the procedure have any influence on the result. For that purpose samples have been heated up to 1100°C in UHV and checked for surface
roughness in situ. The pattern showed the usual 7x7-superstructure and no oscillation of the halfwidths of any spot. Therefore at the beginning the samples were free of steps within the limits of the experiments. Such a sample was treated like a sample etched in HF, to see if any roughness occurs. Starting in UHV, the atmospheric impacts were gradually increased: 1) A short shift into the lock at 5 x 10^{-6} mbar and back to UHV. 2) Exposure to nitrogen within the lock up to 10^{-1} mbar. 3) Exposure to 1 bar of nitrogen within the lock. 4) Exposure to air for 15 sec in the lock. 5) Dipping into methanol after exposure to air and transfer back to vacuum with a droplet of methanol. After each step the sample was transferred back to UHV, checked for roughness and annealed at 1100°C before the next step.

As a result each of the five steps given above increases the background more and more from step one to step five and decreases the intensities within the spots. Up to step 4 the spots are still visible. They do not show any broadening compared to the well annealed structure. Therefore no atomic steps are produced by the parts of the procedure described above.

As a next step the well annealed sample has been brought from the methanol dip into HF and then treated as usual (transfer under methanol into UHV). The result is shown in fig. 4. The lower line gives the instrumental limit. The crosses are the experimental points and the upper line is a calculated curve for a half width of 2.7%, corresponding to an edge atom density of 3.8%. Seven runs yielded similar values. Somewhat lower values have been obtained, when the lock was filled back to atmospheric pressure by nitrogen instead of air.

This residual roughness is considerably lower than that observed for an oxidized sample. An example is shown in
fig. 5. Whereas the oxidized surface (30 sec at 1000° C in dry oxygen) showed a half width of about 12%, (crosses ×, upper line), the same sample yields after annealing to 1000° C in ultra high vacuum a smooth curve without oscillations (circles, lower line). After bringing back to air and an etch in HF as described above a small half width of 3% is observed (crosses +++ and middle line).

These experiments show, that the procedures have a low influence on the observed roughness. It is therefore concluded, that the reported results are due to the interface and not due to handling after etching.

c) Influence of multiple etching, of stains and of storage in air

If the roughness as measured after oxidation is not produced by the etching procedures, it should not be affected by repetition of the etching. For that proof, an oxidized sample (16 h at 1000° C in dry oxygen) has been measured. Fig. 6 shows the half width immediately after removal of the oxide, and the same sample after transfer out of the system into HF and back to the system and after a second repetition of the procedure of etching in HF. It is seen that the half width is always 11.7% ± 0.5%. The results show that repeated etching does not influence the measured half width of an oxidized sample. After annealing of the sample and repeating the etching procedure again a very low half width of 3% (circles in fig. 6) has been found.

Sometimes due to a less careful handling of the samples before oxidation the oxides showed stains and a local variation of the oxide thickness. Those samples showed both a high average half width and a high variation of it over the sample (see fig. 7, upper curve). Those samples
have been disregarded for further evaluations.

A sample, well annealed in UHV has been stored in air over night. Due to that light oxidation (the thickness has not been determined) a small roughness has been observed (see Fig. 7, lower curve, relative half width 5,1 ± 0,7%). A thin oxide therefore produces only a low roughness.

d) Variation of the etching procedure

In all experiments the samples were mounted on the sample holder (out of silicon), dipped together with the sample into methanol and then with a coverage of methanol transferred into the etchant HF. It has been checked, if the coverage with methanol during transfer into the etchant is important.

Therefore for several identically oxidized pairs of samples one sample has been etched with a methanol coverage, the other without it. The results for seven different oxidation parameters are shown in fig. 8. Always the circles refer to etching without methanol and the crosses to etching with it. It is clearly seen that the runs without methanol show an appreciable additional roughening due to the etchant. This is especially drastic for the samples six and seven, which have been annealed in nitrogen at 750°C after oxidation. Obviously the reactivity of the etchant is drastically altered by the absence of methanol. Therefore all following results were obtained with dipping into methanol before etching in HF. In this way an additional roughening due to the etching procedure has been avoided.
IV Results

a) Oxidation at 800°C

Two Si(111)-samples had been annealed each time in UHV at 1000°C to the ideal 7x7 superstructure prior to oxidation. After transfer into the quartz tube they were oxidized in dry oxygen at 800°C for various times (1 min to 20 hours). The oxide thickness was determined (as described in section II) by a Tlanski microscope or by Auger Electron Spectroscopy. The half width of the 00-beam in the LEED pattern was measured for several electron energies between 30 and 110 eV. All reported values are averages of many spots at the sample. The error bars are the standard deviations from the average.

Fig. 9 shows the relative half width (reduced by the instrumental broadening) and the calculated step atom density for many different oxide thicknesses. The crosses are results from one sample after repeated oxidations (with annealing before each oxidation), the circles for another sample. The main result is, that for low oxide thickness (< 20 nm) the edge atom density is appreciably higher (25%) than for higher thickness (only 15%). Obviously a change in the oxidation process occurs at about 20 nm. In fig. 9 also results with wet oxygen are reported (symbol W1 and W2). Sample 1 was well annealed before oxidation and sample 2 was oxidized and etched in HF (without transfer into UHV) before final oxidation. Both samples show an appreciable higher roughness.

The results clearly demonstrate, that both the oxide thickness and the atmosphere have a strong influence on the roughness at the interface between oxide and silicon.
b) Oxidation at 1000°C

The results already reported in the Annual Report (March 1979) for oxidation at 1000°C in dry oxygen have been repeated, confirmed and extended down to thicknesses of about 23 nm. For even thinner oxides the oxidation time would have been too short. The results are shown in fig. 10. Considering the error bars and the extended range the roughness may be described as independent of oxide thickness. This roughness is somewhat lower than that observed after oxidation at 800°C in the same thickness range. One sample (W3) has been oxidized in wet oxygen at 1000°C. Again the roughness is considerably higher (fig. 10, symbols W3).

c) Variation of surface condition before oxidation

The so far reported results have been obtained from samples, which were step free before oxidation due to annealing in ultra high vacuum. To find out, if the condition before oxidation influences the result, four different starting conditions have been checked:

1) Factory polished (by Wacker Chemitronic, Burghausen).
2) Chemically etched with CP6.
3) Oxidized at 1000°C and oxide removed by HF.
4) Step free due to annealing in UHV.

All samples were cleaned ultrasonically and oxidized simultaneously at 1000°C for about 2 hours. The half width was measured for two different electron energies and averaged for many positions on the sample. The average values and their standard deviations are shown in fig. 11. It is seen, that an improvement is obtained by chemical etching, an even better improvement by a first oxidation or an annealing in UHV. To confirm the drastic difference of the first and the third starting condition, such samples
have been oxidized simultaneously in a second run. The results are shown at the right edge of fig. 11. Even at a somewhat higher level of roughness the drastic improvement due to the first oxidation again is evident.

d) Posttreatment after oxidation

All so far reported results have been obtained from samples which were measured immediately after oxidation. To see, if a non-oxidizing posttreatment would vary the results, some of the samples out of the second run in section c) (fig. 11) have been treated after oxidation in nitrogen at 750°C for 5 hours. All samples used for fig. 12 were oxidized simultaneously, some only factory polished, some with prior oxidation and removal of oxide. For both groups the posttreatment in nitrogen yields an appreciable decrease of roughness. The smoothing effect of the posttreatment is also seen in the much smaller scattering of the roughness for different positions on the sample.

V Discussion

a) Reliability of the method

The interface between Si and SiO₂ cannot be studied in situ. The oxide has to be removed. It is a question if the roughness found after removal of the oxide is the same as present at the interface. The experiments of section III show, that all parts of the procedure except the etching in HF do not affect the measured roughness. Also multiple etching did not vary the result. Since it is not possible
to check an etching in HF of an absolutely oxide free silicon surface (any handling at atmospheric pressure produces some minor oxidation), it is only very likely although not proven to the final point, that the procedure does not alter the roughness at the interface. Some results support the conclusion, that the surface under investigation is the wanted interface with respect to roughness: 1) after minimum oxidation (quick handling in atmospheric pressure, no oxidation on purpose) a minimum roughness is observed. 2) The results are reproducible. 3) The measured roughness depends on all oxidation parameters. 4) The measured increase in roughness for low oxide thickness (see fig. 9) coincides with the thickness range, where the growth kinetics is controlled by reactivity at the interface. The lower roughness is only found for oxides, where the growth is diffusion controlled. The measured roughness therefore supports models of growth kinetics (see also the following section b).

Since so far it is not possible to measure surface roughness on an atomic scale with any other technique, a quantitative check of the reliability of the method cannot be given. The qualitative checks, however, make evident, that the measured roughness is highly relevant for the status of the interface before removal of the oxide.

b) The effect of oxidation parameters

The results demonstrate that the interface show an appreciable number of edge atoms. The average terrace width varies from 6 to 40 atomic distances. After annealing at 1000°C in ultra high vacuum the average terrace width is beyond the limits of the method (more than 100 atomic distances). Therefore the measured roughness is produced during oxidation. The roughness strongly depends on the oxidation parameters. The oxidation process occurs after
diffusion of oxygen through the oxide. Due to random fluctuations the attack may be different at different spots of the surface, so that the interface may switch between several layers of the silicon sample. Therefore random attack in reactivity of oxygen is the roughening factor at the interface, which should pile up to more and more roughness with growing oxide thickness, if there would be no smoothing effect. In the case, there is no or not sufficient supply of oxygen at the interface, a smoothing effect has to occur due to diffusion of oxygen at the interface. Similar to the free silicon surface also at the interface a smooth, step free surface is energetically favored compared to a stepped surface. Any diffusion of oxygen at the interface therefore has to smooth the silicon surface under the oxide, until a step free surface is obtained. Since no step free interface has been found, either equilibrium has not been obtained or equilibrium implies a fairly high number of atomic steps due to the entropy contribution to the Helmholtz energy of equilibrium. By using both the roughening and the smoothing effect the results of section IV may be described congruently: In fig. 9 a decrease of roughness for oxide thickness more than 20 nm is observed. If the oxide thickness is plotted versus the oxidation time a linear increase is observed up to that thickness followed by a square root dependence. This result is in agreement with Deal and Grove (8), who interprete the linear increase as reaction controlled and the square root increase as diffusion controlled. If diffusion through the oxide limits the supply a smoothing at the interface should occur. This is observed with the decrease of the roughness. The further decrease of roughness for oxidation at 1000°C (fig. 10) obviously is due to a higher diffusion at the interface.

A strong support of the smoothing at the interface is given by the result, that any annealing in non-oxidizing
atmosphere yields an additional substantial decrease of roughness (fig. 12). On the other hand oxidation in wet oxygen increases the oxidation rate by more than one order of magnitude. Therefore again the reactivity and therefore the roughening effect is increased compared to the smoothing effect. It is a straightforward consequence, that the roughness has to be higher, as found experimentally (figs. 9 and 10).

The dependence on starting condition (fig. 11) yields an additional important factor. Both structural and chemical differences may be the reason. It is, however, difficult to maintain structural differences (like crystallographic distortions by mechanical polishing) at 800° C or 1000° C, since surface diffusion and recrystalisation should restore an ideal surface very quickly. Chemical differences, especially metal or carbon contamination, should vary the electronic properties and therefore the chemical reactivity at the interface substantially, as found in detail on the free, clean silicon surface. The decreasing roughness in fig. 11 may therefore interpreted as increasing cleanliness to start with. Whereas a factory polished sample should show the highest contamination (due to storage in between), even the chemical etch shows more contamination (as proved with AES). Cleaning in ultra high vacuum and a first oxidation obviously yield the same, sufficient cleaning for the present purpose.

The present results therefore for the first time yield direct information, how oxidation parameters influence the roughness at the interface. It is seen, how the treatment has to be varied to yield a low roughness.
c) Comparison with other techniques

Due to the high importance of the Si-SiO$_2$ interface for the performance of MOS-devices a wide variety of methods and techniques have been developed to study both the structural and the chemical and the electronic properties of the interface. Most of the recent results are found in conference proceedings (9, 10, 11). Those methods like Rutherford scattering (12), AES (13,14), XPS (15,16) and UPS (17), Low energy ion scattering (18), contact angle of a liquid (19), TEM (10, 11, 20, 21) and electronic mobility in the space charge layer indicate the presence of a transition layer the thickness of which is estimated to 0.3 - 5 nm, depending on the methods. Some methods cannot distinguish between a gradual change of the chemical composition within the transition layer and an ondulation of the interface with an asperity height as thickness of the transition layer.

The present results give information strictly on structured properties. Especially the average terrace width or the edge atom density are given, which without further assumption may not be used to calculate a thickness of a transition layer. The information is on an atomic scale and somewhat different in nature compared to other techniques, which measure mostly the average chemical or electronic structure after production or removal of an oxide layer (or part of it).

Nevertheless those methods provide some information on structural properties, especially when the oxide layer is removed by ion milling in many small steps (depth profiling by ion bombardment). Measurements of Johannessen, Spicer and Strausser (13) indicate, that during ion milling a constant transition layers for oxides of 10 to 200 nm thickness. For very thin oxides Wagner and Wilmsen (14) found an increase of the transition layer from 1 to 2.5 nm for oxides from 2 to 4.5 nm. Both results
are compatible with our results, although the kind of information is different. The most severe assumption used is, that the ion bombardment itself does not produce an appreciable transition layer by intermixing of the top layers and random fluctuations of the sputtering yield. A careful experimental and theoretical study of the ion bombarding process by Andersen (22) shows, that a substantial transition layer is present with variations depending on energy and mass of the particles. Therefore a limit in depth resolution in the same range of thickness as the determined transition layer. The effect of ion bombardment on the LEED beam profiling technique has been studied by Schulze (23). Starting with a step free surface of germanium, the ion bombardment produced more steps than ever detected for oxidized silicon samples. The step density has been so high, that it was measurable only after a reduction due to a heat treatment. Even then an extraordinary high density has been found. It is therefore concluded that the transition layer as found during ion bombardment is not the same kind of information as found with the LEED technique.

Another important method for structural information is the transmission electron microscopy. A very thin cross section (10 nm) of an MOS structure is studied directly in the microscope. Blanc and coworkers (20) found a sharp and flat border line between Si and SiO₂ down to the resolution of 1 nm (corresponding to about 3 atomic layers). Krivanek and coworkers (21) demonstrated even with a resolution of 0.3 nm, that the transition is abrupt and that there are steps in distances of about 2 to 4 nm at the surface of silicon (which corresponds to widths of 6 to 12 atomic distances). Those results are in agreement with the results of this paper. Although TEM provides direct information on the presence of steps (even without removal of the oxide). This technique is not suited for routine work and precision determination of the step density due to its extreme effort in sample
preparation and quality in microscopy technique.

Indirectly the presence of steps have been concluded from the electron mobility in inversion layers of MOS structures at high inversion and low temperatures. Cheng and Sullivan (24) showed, that varying the oxidation parameters varies also the roughness.

The present results are compatible with all other reported results. On the other hand the present results provide information on the structure at the interface which are not available with any other technique.

VI Conclusion

LEED studies of the Si-SiO₂ interface after removal of the oxide have shown, that a roughness on an atomic scale is present which has been not detected with any other method. Quantitative evaluation of systematic experiments reveal the dependance of some oxidation parameters: Whereas wet atmosphere, short oxidation times and contaminations at the interface yield a high roughness, a fairly smooth surface is obtained for dry oxygen with step free samples to start with, especially when a posttreatment in non-oxidizing atmosphere is added. The results supplement the numerous investigations on the interface with a wide variety of methods. The presented results now enable a direct check of a correlation between electron mobility and step density which has been indirectly concluded from electrical measurements. Therefore the present results open a new way to understand and improve the technologically important interface Si-SiO₂.
Appendix

**Main-program: HALED2**

```fortran
C HAUPTPROGRAMM
C PROGRAMM ZUR BERECHNUNG DER RELATIVEN HALBWERTSDREIEN:

DIMENSION IBUF(2048)

C EICHUNG DES NORMALREFLEXABSTANDES:

AM=150.0
AB=3.326
NEI=0

C ANFANGSDIALOG

WRITE(7,49) FORMAT(1H 'NEU-EICHEN(0),EINGABE D. ALTEN EICHTF.(1)/')
READ(7,11) KONST
IF(KONST.EQ.1) GOTO 99
WRITE(7,19)
WRITE(7,11)
FORMAT(1H '1. EICHUNG DES NORMALREFLEXABSTANDES'
WRITE(7,11)
FORMAT(1H 'ANZAHL DER EICHMESSUNGEN = ?'
READ(7,12)NEICH
IF(NEICH.EQ.0)NEICH=0
NEIC=0
NEI=NEI+1
WRITE(7,21)
FORMAT(1H 'ELEKTRONENENERGIE = ?'
READ(7,22)MVOLT
FORMAT(I4)
IF(NEICH.EQ.0)NEICH=0
NEIC=0

C ANFANGSDIALOG

WRITE(7,10)
FORMAT(1H 'MESSKURVE/ENANZAHL = ?'
READ(7,20) NMESS
IF(NMESS.EQ.0) NMESS=1
IF(NMESS.GT.100) NMESS=1
DO 30 I=1,2048
IBUF(I)=0
30 C EINGABE DES MULTIPLIKATORS FUER INTEGRATIONSZEIT
C ZEIT=ITIME*80MSEC
WRITE(7,49)
FORMAT(1H '80MSEC ? =/
READ(7,50) ITIME
IF(ITAL.EQ.0) ITIME=1
IF(ITAL.GT.50) ITIME=1
C BEGINN DES MESSZYKLUS
CALL TM109(NMESS,ITIME,IBUF)
C AUSGABE DES SPEICHERS
DO 18 I=1,2048
18 IBUF(I)=IBUF(I)/NMESS
IF(REAL(NMESS)/2.0-FLOAT(NMESS/2).EQ.0.0) GOTO 99
DO 99 I=1,2048,1
99 IX=IX+2
IY=IBUF(I)*16
CALL SUBR1(IX,IY)
```

0053  99  CONTINUE
0054  00  CALL  MAXIM(IBUTF,10,2038,MAF,MAA)
0055  05  WRITE(7,3)MAF,MAA
0056  5   FORMAT(1H,'1.MAXIMUM:  MAF - ',I4,'  MAA - ',I4)
0057   N=M9AX1+209
0058  23  N=N+1
0059  60  M1=IBUTF(N)
0060  61  M2=IBUTF(N+1)
0061  62  IF(M1.GE.M2)GOTO 23
0062  64  M3=IBUTF(N+2)
0063  65  IF(M1.GE.M3)GOTO 23
0064  67  IF(N+2.GE.2038)GOTO 24
0065  69  CALL  MAXIM(IBUTF,N+2,2038,MAF,MAA)
0066  70  MAF=MAF
0067  71  MAA=MAA
0068  72  N=N+2
0069  73  WRITE(7,9)
0070  9   FORMAT(1H,'ARG.0B.REL.MIN.  FUN.0B.REL.MAX.  ARG.0B.REL.MIX.')
0071  75  WRITE(7,4)N,MAF,MAA
0072   4  FORMAT(1H,'IS,  'IS,'  'IS,'  'IS,')
0073  76  N=M9AX1-200
0074  26  N=N-1
0075  79  M1=IBUTF(N)
0076  80  M2=IBUTF(N-1)
0077  81  IF(M1.GE.M2)GOTO 26
0078  83  M3=IBUTF(N-2)
0079  84  IF(M1.GE.M3)GOTO 26
0080  86  IF(N-2.LE.10)GOTO 24
0081  88  CALL  MAXIM(IBUTF,10,N-2,MAF,MAA)
0082  89  MAF=MAF
0083  90  MAA=MAA
0084  91  N=N-2
0085  92  WRITE(7,39)
0086  39  FORMAT(1H,'ARG.UN.REL.MIN.  FUN.UN.REL.MAX.  ARG.UN.REL.MIX.')
0087  94  WRITE(7,5)N,MAF,MAA
0088  95  5  FORMAT(1H,'IS,  'IS,'  'IS,'  'IS,')
0089  96  MAA2=MAA1
0090  97  IF(MAF.GT.MAFU)MAAX2=MAA0
0091  99  NXY=1ABS(MAX1-MAAX2)
0092  00  WRITE(7,6)NXY
0093  01  6  FORMAT(1H,'ABS.ANG DER REFLEXE : ',I5)
0094  02  XY=FLOAT(NXY)
0095  03  VOLT=FLOAT(MVOLT)
0096  04  NEIC=NEIC+1
0097  05  YZ=XY*AB*SORT(VOLT/AM)
0098  06  WRITE(7,31)YZ
0099  07  31  FORMAT(1H,'EICHUNG : Y(CL) = ',F8.2)
0100  08  YCL=YCL+YZ
0101  09  GOTO 13
0102  10  13  WRITE(7,33)
0103  11  33  FORMAT(1H,'REFLEXE ZU NAHE AN DEN FELDGRENZEN')
FORTRAN IV

0112  13 CONTINUE
0113  IF (NEI.NE.NEICH) GOTO 14
0115  EIC = FLOAT(NEIC)
0116  YCLM = YCL / EIC
0117  WRITE(7,99) YCLM
0118  29 FORMAT(1H 'EICHUNG:MITTELW.:YCLM - 'F8.2)
0119  YCLA = YCLM * SORT(AN) / AB
0120  WRITE(7,99) YCLA
0121  59 FORMAT(1H 'EICHKONSTANTE : YCLA - 'F8.2)
0122  GOTO 77
C EINGABE DER ALTEN EICHKONSTANTE, DA DER RECHNER
C AUSGESTIEGEN IST
0123  88 WRITE(7,99)
0124  69 FORMAT(1H 'EINGABE DER ALTEN EICHKONSTANTEN')
0125  READ(7,120) YCLAI
0126  51 FORMAT(F8.2)
0127  YCLA = YCLAI
0128  77 CONTINUE
C PROBELAUF: PROGRAMMTEIL ZUR BERECHNUNG DER
C POSITION DES AUSZUKESSENDE倒 REFLEXES
C MESSPROGRAMM FUER TRANSIENTENREKORDER
C ANFANGSDIALOG
0129  WRITE(7,111)
0130  111 FORMAT(1H 'REST. DES MESSINTERVALLES: MESSKURVENANZAHL - ')
0131  READ(7,120) NMESS
0132  120 FORMAT(I4)
0133  IF (NMES.SEQ.0) NMESS = 1
0135  DO 130 I = 1, 2048
0136  130 IBUF(I) = 0
C EINGABE DES MULTIPLIKATORS FUER INTEGRATIONSZEIT
C ZEIT = TIME * 50MSecs
0137  WRITE(7,140)
0138  140 FORMAT(1H '50MSecs ? = ')
0139  READ(7,150) ITIME
0140  150 FORMAT(I3)
0141  IF (ITIME.EQ.0) ITIME = 1
C BEGINN DES MESSZYKLUS
0143  CALL TM109(NMESS,ITIME,IBUF)
C NORMIERUNG DES SPEICHERS
0144  DO 160 I = 1, 2046
0145  160 IBUF(I) = IBUF(I) / NMESS
0146  CALL MAXIM(IBUF, 10, 2038, MAF, MAA)
0147  WRITE(7,102) MAF, MAA
0148  102 FORMAT(1H 'MAX. DES REFL.: MAF = 'F5.1', MAA = 'F5.1)
0149  NOG = MAA + 200
0150  NUG = MAA - 200
0151  WRITE(7,103) NOG, NUG
0152  103 FORMAT(1H 'NOG = 'F5.1', NUG = 'F5.1)
C PROGEEAMTEIL ZUR BERECHNUNG DER
C RELATIVEN HALBWERTS BREITEN--MESSEN--
0153  WRITE(7,211)
0154  211 FORMAT(1H 'MESSEN')
C MESSPROGRAMM FÜR TRANSIENTENREKORDER
C ANFANGSDIALOG

C EINGABE DES MULTIPLIKATORS FÜR INTEGRATIONSZEIT
C ZEIT=ITIME*80MSEC

C BEGINN DES MESSZYKlus
CALL TM109(NMESS,ITIME,IBUF)
C NORMIERUNG DES SPEICHERS
DO 268 I=1,2048
IBUF(I)=IBUF(I)/NMESS
C BESTIMMUNG DES MAXIMUMS IM INTERVALL
CALL MAXIM(IBUF,NUG,NOG,MAF,MAA)
MAFY=MAF
MAYA=MAA
WRITE(7,201)MAF,MAA
C BESTIMMUNG DES ABSOLUTEN MINIMUMS
NUG1=MAAX-500
NOG1=MAAX+500
CALL MINIM(IBUF,NUG1,NOG1,MIF,MIA)
MIFY=MIF
MIAX=MIN
WRITE(7,202)MIF,MIA
C BERECHNUNG DES UNTERGRUNDIES
ADELT=FLOAT(MAF-MIFY)
A6PR=6.0*ADELT/100.0
C ZÄHLUNG ALLER FUNKTIONSWERTE, DIE IM FENSTER
C MINIMUM +6% LIEGEN
A6GR=FLOAT(MIFY)+A6PR
SUM=0.0
M=0
DO 243 I=NUG1,NOG1
```fortran
0202 \texttt{AN=FLOAT(IBUF(I))}
0203 \texttt{IF(AN.GT.1.666) GOTO 243}
0205 \texttt{M=M+1}
0206 \texttt{SUM=SUM+AN}
0207 243 \texttt{CONTINUE}
0208 \texttt{UNT=SUM/FLOAT(M)}
0209 \texttt{WRITE(7,203)UNT}
0210 203 \texttt{FORMAT(1H,'LUETGRAF - ',F9.2)}
0211 \texttt{C MAXIMUM-LUETGRUNDE - DIF2=DIFF/2}
0212 \texttt{DIF2=(FLOAT(MAFY)-UNT)/2.0}
0213 \texttt{C BESTIMMUNG DER GEMESSENEN HALBWERTSBREITE}
0214 \texttt{C OBERER WERT}
0215 \texttt{N=MAAX}
0216 244 \texttt{N=N+1}
0217 \texttt{SX=FLOAT(IBUF(N))}
0218 \texttt{IF(SX-DIF2.GT.0.0) GOTO 244}
0219 \texttt{S1=FLOAT(IBUF(N-1))-DIF2}
0220 \texttt{S2=ABS(S2)}
0221 \texttt{IF(S1.GT.S2) NO=N}
0222 \texttt{NO=N-1}
0223 \texttt{C UNTERER WERT}
0224 \texttt{N=MAAX}
0225 255 \texttt{N=N-1}
0226 \texttt{SX=FLOAT(IBUF(N))}
0227 \texttt{IF(SX-DIF2.GT.0.0) GOTO 255}
0228 \texttt{S1=FLOAT(IBUF(N+1))-DIF2}
0229 \texttt{S2=FLOAT(IBUF(N))-DIF2}
0230 \texttt{S2=ABS(S2)}
0231 \texttt{IF(S1.GT.S2) NU=N}
0232 \texttt{NU=N+1}
0233 \texttt{WRITE(7,204) NU,NO}
0234 204 \texttt{FORMAT(1H,NU=','I5,', NO=','I5)}
0235 \texttt{C BESTIMMUNG DER GEMESSENEN HALBWERTSBREITE}
0236 \texttt{AHBR=FLOAT(NO-NU)}
0237 \texttt{VOL=FLOAT(MVOL)}
0238 \texttt{C BESTIMMUNG DER RELATIVEN HALBWERTSBREITE}
0239 \texttt{RHBR=SQRT(MVOL)*AHBR*100.0/YCLA}
0240 \texttt{WRITE(7,205)MVOL,RHBR}
0241 205 \texttt{FORMAT(1H,'ENERGIE = ','I4,',' EV REL.HALBWBR. = ','F5.2,',')}
0242 \texttt{IF(FLOAT(NMESS)/2.0-FLOAT(NMESS/2).EQ.0.0) GOTO 222}
0243 \texttt{C AUSGABE DES SPEICHERS}
0244 \texttt{DO 262 I=1,2048,1}
0245 \texttt{IX=I*2}
0246 \texttt{IY=IBUF(I)*16}
0247 \texttt{CALL SUBR1(IX,IY)}
0248 262 \texttt{CONTINUE}
0249 \texttt{GOTO 222}
0250 \texttt{STOP}
0251 \texttt{END}
```
SUBROUTINE MAXIM(IBUF,NUN,NOB,MAF,MAA)
DIMENSION IBUF(20)

MAF=0
DO 1 I=NUN,NOB
MAF1=IBUF(I)
IF(MAF1.LE.MAF) GOTO 1
MAF=MAF1
MAA=I
1 CONTINUE
RETURN
END

SUBROUTINE MINIM(IBUF,NUN,NOB,MIF,MIN)
DIMENSION IBUF(20)

MIF=256
DO 2 I=NUN,NOB
MIF1=IBUF(I)
IF(MIF1.GT.MIF) GOTO 2
MIF=MIF1
MIN=I
2 CONTINUE
RETURN
END
Macro Subroutine: TM109

TM109 RT-11 MACRO VM02-12 11-JAN-80 02:59:14 "AGE 1

1 .TITLE TM109
2 .GLOBAL TM109
3 .MCALL ..V2..,REGDEF
4 167760 STATUS=167760
5 167762 OUTP=STATUS+2
6 167764 INF=STATUS+4
7 000000 ..V2..,REGDEF
8 000000 .REGDEF
9 000000 .BLKW 1 ;ADERESE VAN IBUF(1)
10 00002 ITIME: ..BLKW 1 ;INTEGRATIONSZEIT
11 00004 005725 TM109: TST (R5)+ ;Dummy
12 00006 013504 MOV @(R5)+,R4 ;R4 ENTHÄLT MESSANZAHL
13 00010 013567 MOV @(R5)+,ITIME ;ITIME ENTHÄLT INTEGRATIONSZEIT
14 00014 010567 MOV R5,ADRS ;ANFANGSADRESSE VON IBUF
15 00020 012767 START: MOV $000002,OUTP ;RESET HIGH, TRIGGER LOW
16 00026 042767 BIC $000002,OUTP ;RESET RECORDER BIT 1
17 00034 052767 BIS $000002,OUTP
18 00042 G00240 NOP
19 ;ABFRAGE ERSTES BILD ?
20 00044 032767 1$: BIT $001000,INF ;BIT 9 LESEN
001000 167764'
21 00052 001774 BEQ 1$
22 00054 052767 BIS $000004,OUTP ;START INTEGRATION; BIT 2
000004 167762'
23 00062 016701 MOV ITIME,R1
177714
24 00066 012700 2$: MOV $-8730.,.RO ;WARTESCHLEIFE
156746
25 00072 005200 3$: INC .R0
26 00074 002776 BLT 3$
27 00076 005301 DEC .R1
28 00100 001372 BNE 2$
29 ;ABFRAGE VIERTES BILD ?
30 00102 032767 4$: BIT $002000,INF ;BIT 10 LESEN
002000 167764'
31 00110 001774 BEQ 4$
32 00112 042767 BIC $000004,OUTP ;STOP INTEGRATION.BIT 2
000004 147762'
33 ;ABFRAGE ERSTES BILD ?
34 00120 032767 5$: BIT $001000,INF ;BIT 9 LESEN
001000 167764'
35 00126 001774 BEQ 5$
36 00130 032767 BIS $000001,OUTP ;TRIGGERN DES RECORDERS
000001!
TM109  RT-11 MACRO VM02-12  11-JAN-80  02:59:44 PAGE 1+

167762'
37 00136 042767  BIC  $000001,OUTP
000400
167762'
38 00144 000240  NOP
39  ;WARTESCHLEIFE BIS AUFNAHME BEendet IST
40  ;ABFRAGE BIT 9 DES DIGITALEN EINGANGES
41 00146 032767 10$: BIT $000400,INF ;BIT 9 LESEN
000400
167764'
42 00154 001374  BNE  10$
43  ;LESEN DES SPEICHERS
44 00156 000240  NOP
45 00160 012700  MOV  $-2018,RO  ;ZAEHLER SETZEN
174000
46 00164 016701  MOV  ADRS,R1
177610
47 00170 116703 LOOP: MOVB INF,R3
167764'
48 00174 042703  BIC  $177400,R3
177400
49 00200 060321  ADD  R3,(R1)+
50 00202 005200  INC  R0
51 00204 001371  BNE  LOOP
52 00206 005304  DEC  R4  ;INMESS HERABSETZEN
53 00210 001303  BNE  START
54 00212 000207  RTS  PC  ;BACK TO PROGRAMM
55 000004'  END  TM109

TM109  RT-11 MACRO VM02-12  11-JAN-80  02:59:44 PAGE 1+

SYMBOL TABLE

ADR S  000000 R  IN P  =  167764  ITIME  000002 R
000000 R  OUT P  =  167762  PC  =  000002
R0  =  000000  R1  =  000001  R2  =  000002
R3  =  000003  R4  =  000004  R5  =  000005
SP  =  000006  START  =  000020 R  STATUS  =  167760
TM109  000004 R  ...V2  =  000001
*  ABS  000000  000  000214  001

ERRORS DETECTED: 0
FREE CORE: 17658. WORDS

TM109,TT:=TM109

ERRORS DETECTED: 0
FREE CORE: 17658. WORDS

*
Macro Subroutine: SUBR1

.RU DX1:MACRO
*SUBR1,TT:=SUBR1
SUBR1 RT-11 MACRO VM02-12 11-JAN-80 03:07:09 PAGE 1

1 .TITLE SUBR1
2 .GLOBL SUBR1
3 .MCALL .V2...
4 170420 REGISX=170420
5 170422 REGISY=170422
6 000000 .V2...
7 000000 .REGDEF
8 000000 005725 SUBR1: TST (R5)+
9 000002 013567 MOV @(R5)+,REGISX
10 00006 017367 MDV @(R5),REGISy
170422 000000
170422
11 ;SPEICHERINHALT IST IM AUSGABEREGISTER
12 ;WAIT A LITTLE
13 00014 012700 MOV R0-1000.,RO
176030
14 00020 005200 INC R0
15 00022 003776 BLE 1$
16 00024 000207 RTS PC ;ZURUECK ZUM HAUPTPROGRAMM
17 000000 .END SUBR1

SYMBOL TABLE

PC =%000007 REGISX= 170420 REGISY= 170422
R0 =%000000 R1 =%000001 R2 =%000002
R3 =%000003 R4 =%000004 R5 =%000005
SP =%000006 SUBR1 000000RG ...V2 = 000001

* ABS. 000000 000 00026 001
ERRORS DETECTED: 0
FREE CORE: 17698. WORDS

SUBR1,TT:=SUBR1

ERRORS DETECTED: 0
FREE CORE: 17698. WORDS

*
References

22. H.H. Andersen, Appl. Phys. 18, (1979) 131
23. G. Schulze, M. Henzler, Surface Sci. 73 (1978) 553
Figure Captions

Fig. 1: Schematic configuration of LEED and closed TV-system

Fig. 2: Examples for oxide thickness determination with Auger electron spectroscopy
a) Spectrum of a clean silicon surface
b) Si with a layer of about 2.7 nm SiO₂
c) Si with a layer of SiO₂ larger than 12 nm

Fig. 3: a) Auger spectrum of a crystal directly after removal of the oxide and transfer in the UHV
b) Auger spectrum of the sample holder after several experimental cycles

Fig. 4: Relative half width of the 00-spot versus energy for a well annealed probe (7x7) structure, etched in HF and transferred back to UHV. The upper curve is calculated for an edge atom density of 3.8% and is the best for the experimental points (crosses). The lower curve gives the instrumental limit. S (an multiples of 2π) indicates the energies at which in-phase scattering happens.

Fig. 5: Relative half width versus energy for the same sample after the following treatments:
a) Oxidation 30 sec at 1000°C in dry oxygen (crosses xxx) upper curve calculated for a half width of about 12%
b) Annealing at 1000°C (7x7 structure), yielding instrumental limit (lower curve, circles OOO).
c) Annealing at 1000°C, transfer to atmosphere, etching in HF, transfer back to UHV, showing a residual roughness (center curve: crosses +++).
Fig. 6: Relative half width versus energy for the same sample after the following treatments:

a) Oxidation 16 h at 1000°C in dry oxygen, etching in HF (crosses: xxx).

b) Second etching in HF without annealing (crosses: +++).

c) Third etching in HF without annealing (crossed circles: 000).

d) Etching in HF after annealing at 1000°C. Upper curve is calculated for a half width of about 11.7%, center curve for 3%.

Fig. 7: Corrected relative half width and step atom density versus position on the crystal for a sample with a wide scatter of oxide thickness (upper curve) and a sample with a light oxidation (overnight at room atmosphere, lower curve).

Fig. 8: Corrected relative half width and step atom density versus various oxidation pre- (1. - 5.) and posttreatment (6, 7) procedures

a) with dipping into Methanol before etching in HF (crosses: xxx)

b) without dipping into Methanol before etching in HF (circles: 000)

Oxidation parameters: 2 hours at 1000°C in dry oxygen

Fig. 9: Corrected relative half width and step atom density versus oxide thickness for two samples (crosses: x and circles: 0), which were well annealed in UHV (7x7 structure) before oxidation at 800°C in dry oxygen.

Sample W1 (pretreatment: annealing in UHV), and sample W2 (pretreatment: oxidized and etched in HF) were oxidized in wet atmosphere.
Fig. 10: Corrected relative half width and step atom density versus oxide thickness for samples (crosses: xx) oxidized at 1000°C in dry atmosphere. Sample W3 has been oxidized in wet oxygen.

Fig. 11: Corrected relative half width and step atom density versus treatment before oxidation (2 h at 1000°C in dry oxygen)

1. Factory polished (by Wacker Chemitronic, Burghausen) (crosses: xxx).
2. Chemically etched with CP6 (circles: OOO).
3. Oxidized at 1000°C and oxide removed by HF (crossed circles: @@@)
4. Step free due to annealing in UHV (crossed circles: @@@)

1' and 3' indicates a second experimental run with the same treatment as in 1. und 3.

Fig. 12: Corrected relative half width and step atom density versus treatment before and after oxidation (2 hours at 1000°C in dry oxygen)

1. Factory polished
1' With additional annealing (5 hours in N₂ at 750°C)
3. Oxidized at 1000°C and oxide removed by HF before oxidation
3' With additional annealing (5 hours in N₂ at 750°C)
Fig. 1

LEED - system

window

crystal

monitor

camera control

ADC
transient recorder
DAC

XY-recorder

TV - camera

computer:
PDP 11

terminal
Ep = 6.6 kV
Ip = 5 µA
V_{MOD} = 2 V
V_{MULT} = 1.8 kV
RC = 1 s

a) pure Si

~ 27 Å Si O₂

b) \( I_{SiO₂} \approx 0.86 \)
\( \frac{I_{SiO₂}}{I_{Si}} \approx 1 \)

c) Si O₂ > 120 Å

Fig. 2
$E_p = 5 \, \text{kV}$

$I_p = 5 \, \mu\text{A}$

$V_{\text{MOD}} = 2 \, \text{V}$

$V_{\text{MULT}} = 1.7 \, \text{kV}$

$RC. = 0.3 \, \text{s}$

Fig. 3
Relative half-width

Fig. 5

Electron energy

S = 1, 2, 3, 4, 5
position on crystal:

Fig. 7
corrected relative half-width

various oxidation and pretreatment procedures

Fig. 8
![Figure 12](image)

<table>
<thead>
<tr>
<th>Step Atom Density (corrected relative half-width)</th>
<th>N₂ Annealing</th>
<th>HF Oxide</th>
<th>N₂ Annealing</th>
<th>Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement Before and After Treatment</td>
<td>0</td>
<td>15</td>
<td>15</td>
<td>30%</td>
</tr>
</tbody>
</table>