

01 Jan 1972

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Recommended Citation

L. E. Davis et al., "A Study Of Phosphorus Adsorption And Desorption Kinetics On Silicon (111) Surfaces," *Journal of Crystal Growth*, vol. 17, pp. 354 - 356, Elsevier, Jan 1972.

The definitive version is available at [https://doi.org/10.1016/0022-0248\(72\)90269-2](https://doi.org/10.1016/0022-0248(72)90269-2)

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A STUDY OF PHOSPHORUS ADSORPTION AND DESORPTION KINETICS ON SILICON (111) SURFACES

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Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) methods were used to characterize the (111) surface of Si wafers before and after the deposition of P_2 molecules. Before deposition, the well-known Si(111)-7 LEED pattern was easily obtained by thermal cleaning at 1200 °C. Cleaning was done by electron bombardment in a vacuum chamber with a base pressure of $\sim 10^{-10}$ Torr. After cleaning, AES showed that about 10^{-2} atomic layer of carbon was the only surface contaminant. The sensitivity of our cylindrical AES apparatus for phosphorus was about 10^{-3} atomic layer. We found that $\sim 5 \times 10^{-2}$ atomic layer of phosphorus deposited on a Si(111) surface caused the fractional order spots to disappear from the LEED pattern, so that a sharp Si(111)-1 pattern remained. The kinetics of phosphorus desorption from the Si(111) surface was investigated with AES and mass spectrometry. P_2 was found to be the main desorption product. The desorption process obeyed second order kinetics. The activation energy for the desorption of P_2 was 68.6 ± 0.8 kcal mole $^{-1}$ for phosphorus coverages between 0.1 and 0.5 atomic layer.

1. Introduction

The main purpose of the present study was to determine the nature of phosphorus bonding to a clean Si(111) surface. In this study we have used Auger electron spectroscopy (AES) to quantitatively evaluate the thermal desorption kinetics as opposed to the more usual methods (see refs. 1 and 2 for review articles) of determining the desorption rate with a mass spectrometer. In a previous study³), the quantitative correlation of phosphorus coverage with the phosphorus Auger electron signal had been made. Hence, AES has been used here [as in the study of Florio and Robertson⁴)] to continuously monitor the surface coverage of phosphorus during heat treatment of the silicon. Low energy electron diffraction (LEED) also was used in the hope that a model for the proper positioning of the phosphorus atoms or molecules would be indicated.

2. Experimental apparatus and procedure

The experiments were performed inside a stainless steel vacuum chamber which could be evacuated to pressures $\leq 1 \times 10^{-10}$ Torr. The main residual gases present, as detected by a monopole mass spectrometer, were H_2 ($P_{H_2} \simeq \frac{1}{2} P_{CO}$), CO and CO_2 ($P_{CO_2} \simeq \frac{1}{2} P_{CO}$). Pressures $\leq 2 \times 10^{-9}$ Torr were maintained during the heating of the silicon wafer or during the evaporation of phosphorus.

The experimental arrangement is shown in fig. 1. The 16 mm diameter, 0.5 mm thick silicon sample (resistivity > 1000 ohm-cm) was mounted on a vacuum manipulator. With this arrangement, the sample could be placed in front of the AES optics (cylindrical velocity analyzer with coaxial electron beam), the phosphorus evaporation source, or the mass spectrometer.

The silicon sample was heated by electron bombard-

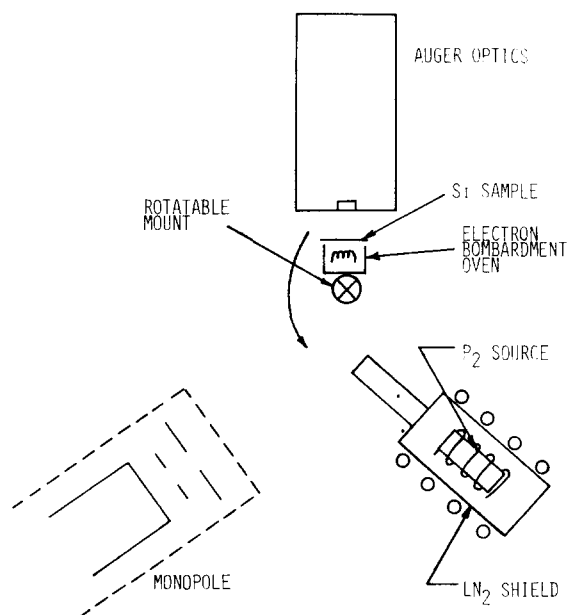


Fig. 1. Schematic diagram of the experimental arrangement.

ment. The bombardment oven was placed directly behind the sample. The oven and sample were mounted on the same manipulator. Temperature measurements were made by a thermocouple (in contact with the sample) and by infrared and optical pyrometers through a vacuum window. Initial cleaning of the sample was accomplished by heating at 1200 °C for several minutes. Subsequent cleaning was possible at lower temperatures and shorter time intervals. After cleaning, LEED (LEED optics not shown in fig. 1) patterns of the well-recognized Si(111)-7 structure were observed. The AES scan of the clean sample (fig. 2a) revealed that carbon [estimated coverage 0.05 monolayer³] was the only remaining impurity. Fig. 2a shows the Auger spectrum of silicon before the deposition of phosphorus. LEED patterns were also observed with various amounts of phosphorus on the Si(111) surface, as measured by AES.

The phosphorus evaporation source, already described^{3,5}), is a source of diatomic phosphorus. Therefore, in our study, the phosphorus was deposited on the Si surface as P₂. An initial coverage of approximately

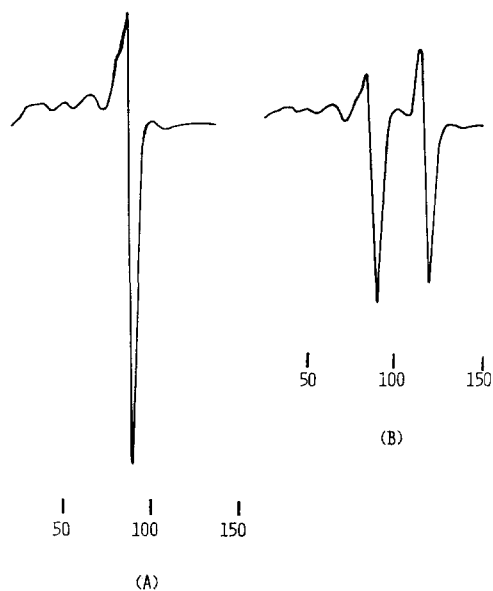


Fig. 2. Auger spectra [$dN^-(E)/dE$] of the Si (111) surface. (A) Thermally cleaned silicon; (B) after evaporation of approximately 7.5×10^{14} atoms/cm² of phosphorus (121 eV).

7.5×10^{14} atoms cm⁻² was used for the desorption studies. This corresponded to nearly one monolayer of phosphorus, as determined from the Auger electron spectrum. Fig. 2b shows the Auger spectrum taken with

the initial phosphorus coverage. Both curves in fig. 2 were obtained with the same settings on the AES instrumentation.

Although the desorption kinetics results presented here were obtained with AES, mass spectrometric studies were also made. These revealed that the phosphorus desorbed predominantly in the molecular form of P₂.

After the phosphorus layer was deposited and characterized, the sample was heated to a fixed temperature T . During heating, the phosphorus Auger electron signal S was continuously monitored as

$$S = dN^-(E)/dE, \quad (1)$$

where $N^-(E)$ is the number of electrons at a given energy E . Here S is the signal recorded at the electron energy E of 121 eV, which corresponded to the minimum of dN^-/dE . Since the shape of the phosphorus Auger signal does not change with coverage^{3,6}) it follows that

$$S = \theta S_{\theta=1}, \quad (2)$$

where θ is the fraction of one monolayer coverage. From the measured population density $N_{\theta=1}$ (atoms cm⁻²), at monolayer coverage, we could determine N_{θ} as a function of S . The rate of desorption \dot{N}_{θ} (atoms cm⁻² sec⁻¹) was then determined from measurements of dS/dt , the rate of change of the phosphorus Auger electron signal.

3. Experimental results

3.1. LEED

Beginning with a clean Si(111)-7 diffraction pattern, it was observed that the fractional order diffraction beams of the Si(111)-7 disappear at about 0.05 monolayer of phosphorus to form a Si(111)-1-P structure. This structure does not change with increasing coverage, but above one monolayer the diffraction beams are very low in intensity. At 3–4 monolayers, all diffraction beams are completely extinguished, indicating amorphous growth of the phosphorus.

Adsorption of phosphorus on silicon at elevated temperatures ($T > 850$ °C) did not change the surface structure (i.e., the LEED pattern was Si(111)-1-P). It is significant that the Si(111)-6-P diffraction pattern for phosphorus-doped silicon reported by Gallon, Prutton and Wray⁷) was not observed in this study.

3.2. AES

The general desorption rate equation for a single surface bond is

$$-\dot{N} = N^n v_n \exp(-E_D/RT), \quad (3)$$

where \dot{N} is the rate (atoms $\text{cm}^{-2} \text{sec}^{-1}$) of desorption, N is the instantaneous concentration (atoms cm^{-2}) of P atoms, E_D is the activation energy of desorption (cal mol^{-1}), $R = 1.987 \text{ cal mol}^{-1} \text{ }^\circ\text{K}^{-1}$, T is the absolute temperature and v_n is the pre-exponential factor for n th order desorption. By measuring the desorption rate at several fixed sample temperatures all parameters are determinable.

Fig. 3 is a typical isotherm ($T = 1140 \pm 10^\circ\text{K}$) of the desorption rate as a function of phosphorus coverage. For all isotherms in the temperature range of 1000 to 1200 $^\circ\text{K}$, the desorption was found to be dominated by a second order process, $n = 2$ (indicated by the slope of fig. 3). At very low coverages ($\theta < 0.1$), there was also an indication that the desorption changes to first order. However, more low coverage data is needed to confirm this.

The activation energy of desorption E_D was deter-

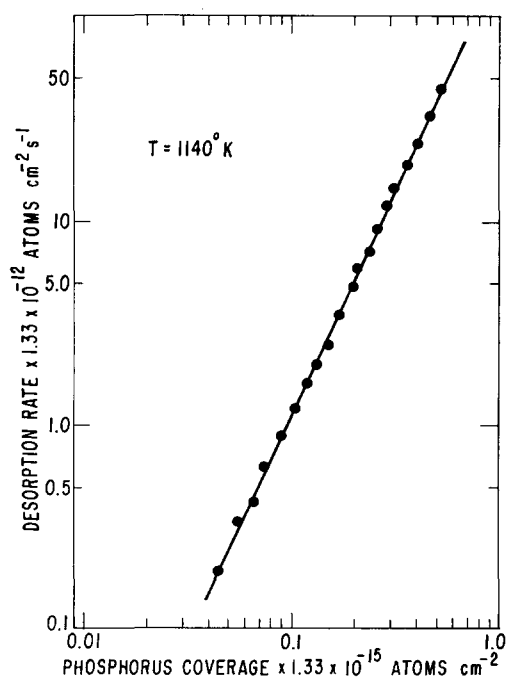


Fig. 3. The desorption rate of phosphorus from silicon as a function of coverage. Slope = $\Delta \log \dot{N} / \Delta \log N = 2.2$.

mined from plots of $\log \dot{N}$ versus $1/T$ for $0.1 < \theta < 0.5$. The value for E_D was found to be $68.6 \pm 0.8 \text{ kcal mol}^{-1}$ in this range of θ . The average value for the pre-exponential factor v_2 was $4 \times 10^{-3} \text{ atoms}^{-1} \text{ sec}^{-1} \text{ cm}^2$.

4. Discussion

The LEED results show that the fractional order beams are extinguished by the deposition of approximately 0.05 monolayer of phosphorus. This indicates that a part of the Si(111) surface is restructured by the presence of a small amount of phosphorus. Weber⁸) has found that Si(111) surfaces having less than 0.01 monolayer of carbon impurity also give the Si(111)-7 LEED pattern. Since our surfaces had carbon impurity levels of 0.05 monolayer, it is clear that the Si(111)-7 pattern does not necessarily indicate a clean surface. Furthermore, it is apparent from these observations that the Si(111) surface structure is dependent on the amount as well as on the type of impurities present.

The desorption kinetics of phosphorus as determined by AES have been shown to be second order. Since it was already known that the adsorbed phosphorus species was P_2 and that the desorbed species is predominantly P_2 ($P_{\text{P}_1} \leq 0.2 P_{\text{P}_2}$), we conclude that P_2 dissociates upon adsorption onto clean silicon and then recombines during desorption.

We have found AES to be much more sensitive in determining desorption kinetics than mass spectrometric methods. Isothermal desorption measurements with a mass spectrometer in this study revealed no kinetic information below a few tenths of a monolayer. Future studies with AES should resolve the desorption kinetics of phosphorus on silicon below 0.1 monolayer. However without mass spectrometric analysis, low coverage data may not reveal much about the surface bonding.

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