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Photodesorption Cleaning of Silicon with Vacuum Ultraviolet Irradiation

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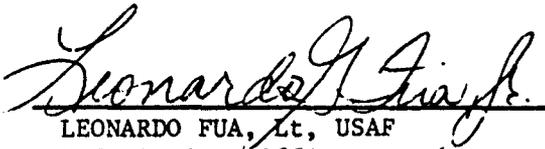
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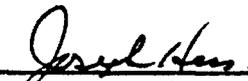
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An investigation into the use of vacuum-ultraviolet irradiation for photodesorption cleaning of the surface of silicon contaminated by carbonyl and hydrocarbon adsorbates has been made.

PREFACE

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FIGURES

1. INTRODUCTION

Carbon-containing compounds adsorb onto cleaned surfaces from ambient air
and in some vacuum chambers [1,2,3,4]. Any operator of an x-ray photoelectron
spectrometer (XPS), Auger spectrometer or secondary ion mass spectrometer
(SIMS) can attest to the ubiquitousness of organic contaminants. Chang and
coworkers [3] discovered that in spite of using exceptional care in the
etching procedures for GaAs, carbon was present after etching and was not
reduced appreciably by the thermal removal of tne oxide layers. The effect of
organic impurities between layers on semiconductor device performance is not
fully known, however, it has been determined that contamination can cause poor
adhesion of Cr/Au metallization to glass [1]. Chang, et al., have measured
increased resistance and nonlinear I-V characteristics as a result of the
presence of carbon between the GaAs substrate and an MBE grown n^+-GaAs film
[3]. Equally damaging to the vertical electron transport properties is the
nonannealable (550°C) increased resistance that results from sputter-cleaning
damage to the substrate surface prior to the growth of the n^+-GaAs film.

The combination of ultraviolet irradiation and ozone has been determined
to be effective for cleaning surfaces as measured by minimization of distilled
water contact angles [1,5]. More sensitive surface analyses such as XPS and
Auger spectroscopy have recently confirmed this method's effectiveness.
However, it is recognized that the strong oxidizing properties of ozone may
prove to be deleterious for some cleaning purposes [5].

Recent studies have revealed a strong correlation between photon energy
in the ultraviolet wavelength region and photodesorption effectiveness [6,7].
These studies did not include wavelengths shorter than 249 nm. However, the
sharp increase in photodesorption signals with decreasing wavelength below
300 nm [7] suggests that wavelengths shorter than 240 nm may be even more
effective in desorption processes.

A newly developed method of photochemical deposition uses the output of vacuum ultraviolet lamps to drive chemical vapor deposition (CVD) reactions [8,9]. A key step in the process (prior to the deposition) is the irradiation of the substrate surface with VUV light (105-190 nm) to volatilize spurious adsorbed material that is then removed by the vacuum system. Evidence of the effectiveness of this photodesorption cleaning step is the chemical bonding of VUV-CVD silicon to the surface of VUV pre-cleaned sapphire (Al_2O_3) and quartz (SiO_2) [9]. This observation led us to investigate the photodesorption process in the vacuum ultraviolet region ($\lambda < 190$ nm) and to evaluate its effectiveness as a pre-cleaning step that may provide damage-free, superior interface properties between layers on semiconductor devices.

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2. EXPERIMENT PROCEDURE

The (100) surface of n-type phosphorous doped silicon (Siltec Corp.
lot #813732) was used for this study. A comparison of the XPS analysis before
and after VUV exposure was made for the silicon as received versus those
surfaces that had been chemically cleaned. The chemical cleaning was done in
our laboratory and included the following steps: 1) 10 min. in warm 1:1
NH_4OH/H_2O_2, 10 min. rinse; 2) 10 min. in warm 1:2 HCl/H_2O_2, 10 min. rinse;
3) 10 sec. in 10% HF, 10 min. rinse and spin dry. The cleaned silicon was
then stored under nitrogen atmosphere at $600^{c}C$ until used. The rinses in all
cases were in 18 MΩ water. For simplicity, the samples that received this
treatment will be referred to as clean samples.

A modified X-ray photoelectron spectrometer (GCA/McPherson ESCA 36) with
a time-integrating, optical position-sensitive detection system (consisting of
a channel electron multiplier array, a Princeton Applied Research model
1205 vidicon camera and an optical multichannel analyzer [10] was used for the
surface analyses before and after VUV exposure. Modifications included the
retrofitting of an Inficon model IQ 200 quadrupole mass spectrometer and our
VUV lamps to the XPS chamber. The modified XPS system is illustrated in
Figure 1. The sample stage, which could be moved from the X-ray source to the
VUV source by an external manipulator arm, allowed XPS analysis before and
after the VUV irradiation without exposure of the sample to the atmosphere.

Two types of in-house designed lamps were used in this study. In the
initial phase, irradiation from the xenon continuum lamp was discovered to be
effective in the photodesorption of a contaminant that contained a carbonyl
structure (C=O). The xenon lamp's emission is in the wavelength region of
147 nm to 190 nm with a peak intensity at 160 nm ($\sim$ 8 eV/photon) [11]. An
argon lamp was used to evaluate the shorter wavelength VUV photodesorption
effectiveness. The emission spectrum of the argon lamp is believed to be
similar to the one in reference 11 which has a peak intensity at 125 nm
($\sim$ 10 eV/photon). The argon lamp's design is similar to that of the xenon
lamp except for the absence of a window on the VUV output end and the addition
of a gas metering valve on the back end.

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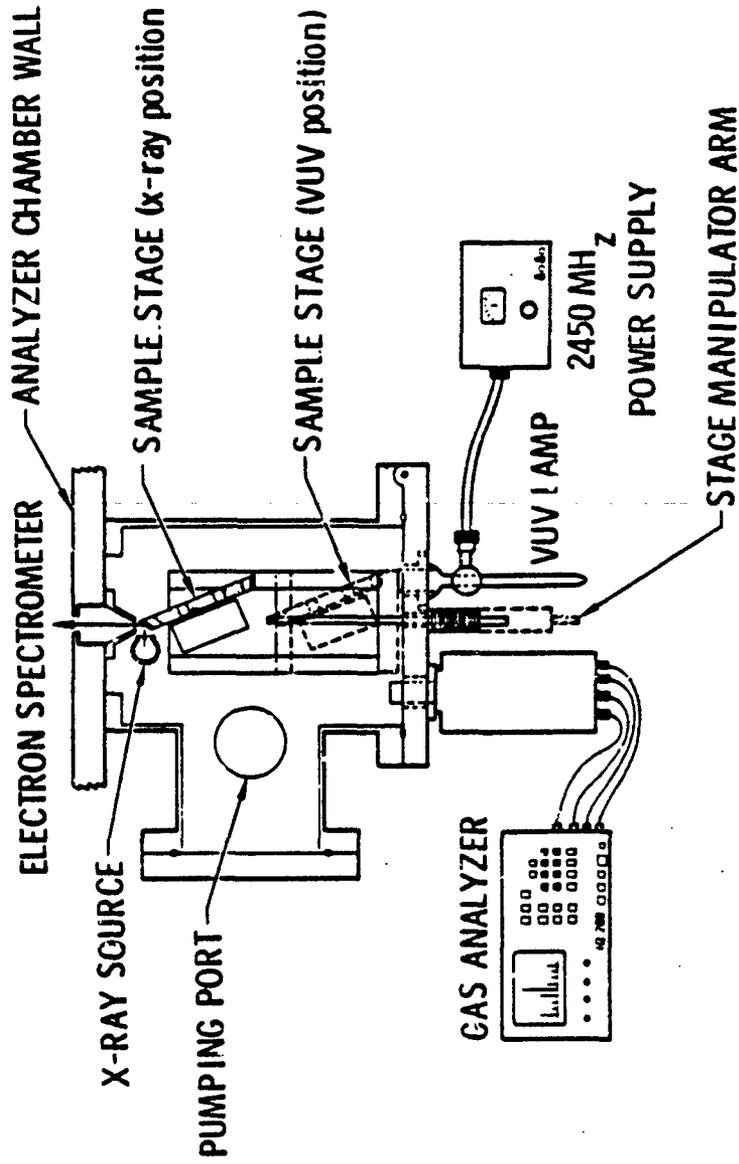
Figure 1. Modified XPS System

The chamber pressure was maintained at 2×10^{-7} torr by a turbomolecular pump and a helium cryo-pump during the XPS analysis and during the sample irradiation with the xenon lamp. The chamber pressure was maintained at 4 torr during the operation of the argon windowless lamp. Argon was flowed through the lamp at 200 cc/min into the XPS chamber and removed at the same rate through a metered valve by a turbomolecular pumping station. After the completion of an irradiation time period, the chamber was evacuated to 2×10^{-7} torr and XPS analysis performed.

Because of the high chamber pressure during the operation of the argon windowless lamp, there was no attempt to record the photodesorption products with the mass spectrometer.

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3. RESULTS AND DISCUSSION

Analysis by XPS has revealed that the surface of silicon becomes contaminated with hydrocarbon (HC) and carbonyl (C=O) structured compounds in a normal laboratory atmosphere. The HC adsorbate levels were ~ 10 times the C=O levels on all samples. Examples of additional compounds that are probably adsorbed but not always detectable by standard XPS analysis are H_2O, O_2 and N_2. Only the compounds detected by our XPS system will be discussed in this report. An XPS spectrum of the surface of cleaned silicon is shown in Figure 2. The peak at 285.0 eV is due to the C(1s) electron in aliphatic hydrocarbons. Figure 3 is an expanded view of this region which reveals a weak shifted band at 288.5 eV. This peak is from the C(1s) electron in a compound that contains a carbonyl structure (C=O). We evaluated the effect of vacuum ultraviolet irradiation on the photodesorption of the HC and C=O adsorbates with respect to time and VUV wavelength.

3.1 PHOTODESORPTION OF CARBONYL COMPOUNDS

The 288.5 eV band was reduced to ~ 50% its original intensity after ten minutes of irradiation with the xenon continuum lamp (~ 8 eV/photon). After 20 minutes of exposure with the xenon lamp, the carbonyl contaminant was reduced to an undetectable level. However, no measurable decrease in the hydrocarbon contamination was detectable after the xenon lamp exposure.

From the XPS analysis, we estimated that the carbonyl contaminant before exposure to VUV irradiation covers approximately 20% of the silicon surface. Assuming that each of the adsorbate molecules occupies a 10 $Å^2$ area, then 2×10^{14} molecules would be adsorbed within a one cm^2 area. Since we measured a 50% decrease in the carbonyl compounds' signal after 10 minutes of irradiation, this would then correspond to ~ 1×10^{14} molecules removed in 600 seconds. Our xenon VUV lamp's output has been calibrated at 2×10^{15} photons/cm^2sec. This means 1.2×10^{18} photons will impinge upon the silicon surface in 600 seconds. From these approximations and the measured lamp output, the 160 nm photodesorption efficiency of the carbonyl adsorbate can be approximated by
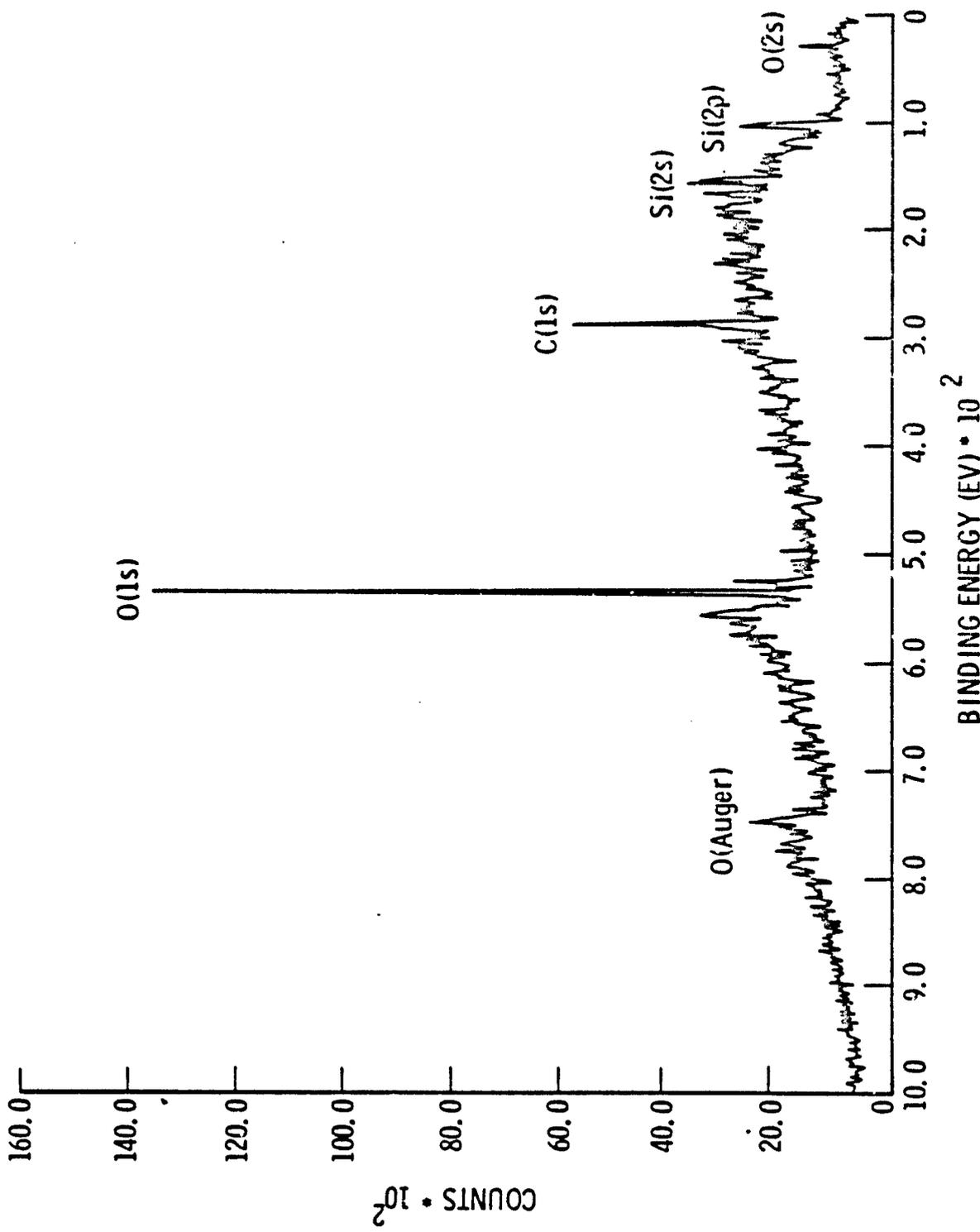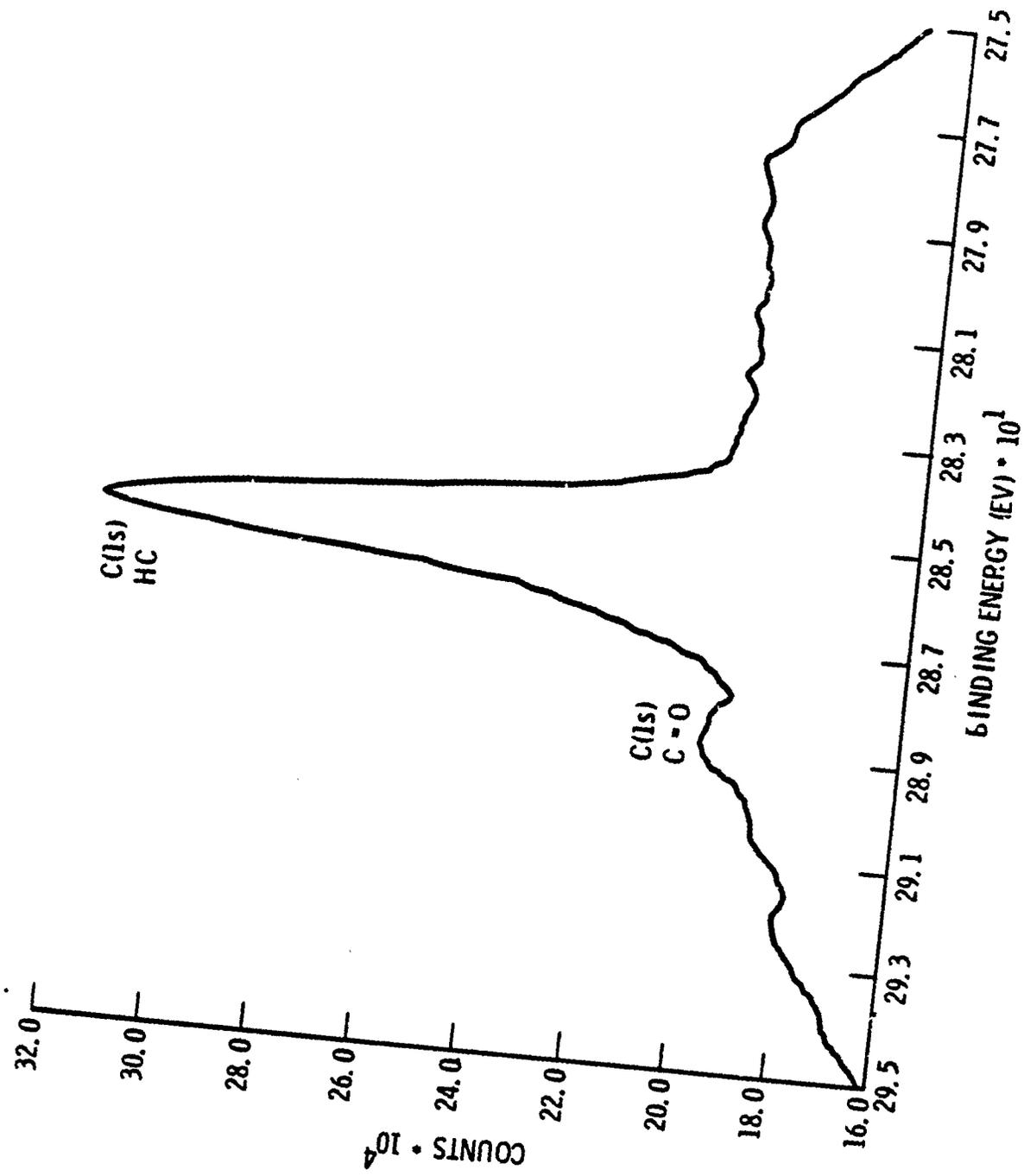
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Figure 2. XP Spectrum of Si Surface

Figure 3. Expanded XPS Spectrum of Si Surface

C(1s)
HC

C(1s)
C - O

BINDING ENERGY (EV) • 10^1

COUNTS • 10^4

$$\phi_d = \frac{Nc}{Np} = 10^{-4}$$

where: ϕ_d = photodesorption efficiency for carbonyl compounds

Nc = number of carbonyl molecules desorbed/sec

Np = number of incident photons/sec

The photodesorption efficiency value of 10^{-4} is a lower limit approximation due to the limited surface coverage by the carbonyl adsorbate compared to the total coverage by the VUV irradiation.

3.2 HYDROCARBON PHOTODESORPTION

There was no measurable reduction in the hydrocarbon (HC) XPS signal after irradiating the silicon surfaces with the output of the xenon lamp. This is believed due to insufficient overlap in the emission spectrum of the xenon lamp with the absorption of aliphatic hydrocarbons in the vacuum ultraviolet region [12]. This problem was overcome by using the windowless argon lamp, which emits at shorter wavelengths. Two minutes of irradiation with the windowless argon lamp reduced the HC on cleaned silicon to 20% of its original XPS intensity. It is interesting to note that during this same period the Si-Si and Si-O photoelectron signals at 99.8 and 103.5 eV both increased slightly (see Figure 4). Thus, VUV irradiation did not disrupt the Si-Si or Si-O bonding, nor did it remove Si from the surface. Assuming a smooth layer and an electron escape depth of ~ 20 Å, the hydrocarbon adsorbates are estimated to be 4 Å thick before irradiation. After irradiation, the layer is thinner, so electrons emitted from the underlying Si can escape the sample more easily, thus causing the observed increase in Si-Si and Si-O signal intensity. An additional seven minutes of irradiation reduced the HC XPS signal to 6% of the original intensity. The sample was then allowed to sit in the XPS chamber at 2×10^{-7} torr for two hours. This resulted in an increase in the HC adsorbates on the VUV-cleaned silicon surface. This increase is believed to be due to adsorption from a residual hydrocarbon vapor pressure in the XPS chamber. Increases in hydrocarbon levels on sample surfaces with time and X-ray exposure in XPS chambers have been observed by others [13]. X-ray exposure does not decrease the hydrocarbon and carbonyl

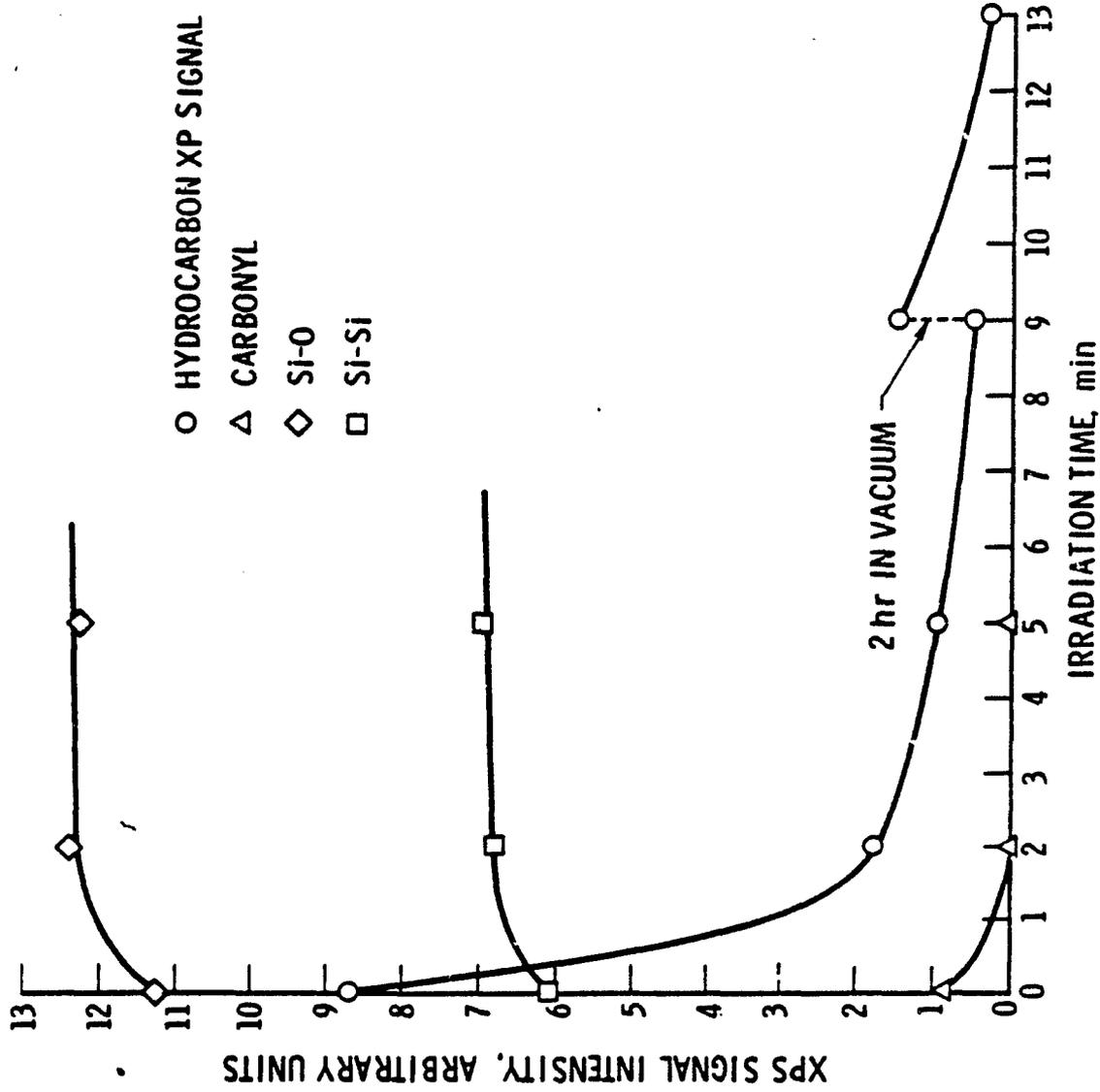Figure 4. Effect of Irradiation on Si-Si, So-O and HC and C=O contaminants

levels even though there is heating of the sample. Nor does exposure of the silicon surface to the same pressure and flow of argon that was used during the VUV irradiation reduce these adsorbates. Only the argon lamp was effective in photodesorbing both the hydrocarbon and carbonyl contaminants from the surface of silicon.

4. CONCLUSIONS

We have determined that the surface of silicon becomes contaminated with hydrocarbon and carbonyl adsorbates in a normal laboratory atmosphere and in a turbomolecular-pumped vacuum system. The adsorbates are strongly bound and are not removed by exposure to X-rays during XPS analysis. However, it was found that the carbonyl adsorbates are removed with 8 eV/photon irradiation and that both the carbonyl and hydrocarbon adsorbates are removed with 10 eV/photon irradiation.

The mass spectrometer was intended to identify the gaseous species as they were photodesorbed by VUV irradiation. For the conditions of this experiment, the volume of the XPS chamber and the pumping speed of the vacuum system were too great to permit this. Additional tests are planned that are expected to overcome these obstacles. .

The 160 nm photodesorption efficiency value of 10^{-4} for carbonyl adsorbates from the surface of silicon is a lower limit approximation for the limited substrate coverages that were observed. It is large when compared to Genequand's value of 10^{-9} for the photodesorption efficiency of CO_2 from the surface of nickel with 253 nm irradiation [14]. Further testing will be required to determine if this large difference is due to more efficient desorption with shorter wavelength light or to photochemical decomposition of the contaminant by the shorter wavelength light.

As hydrocarbon compounds are excellent insulators (e.g., electrical wire insulation), their presence between layers on integrated circuits will tend to increase resistance and make the device less efficient. Additional work will be required to determine if the levels of contamination that we have found to spontaneously adsorb onto the surface of silicon will produce a deleterious effect.

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