LBL-29623
Preprint

Center for Advanced Materials

CAM

Submitted to Journal of Vacuum Science & Technology A

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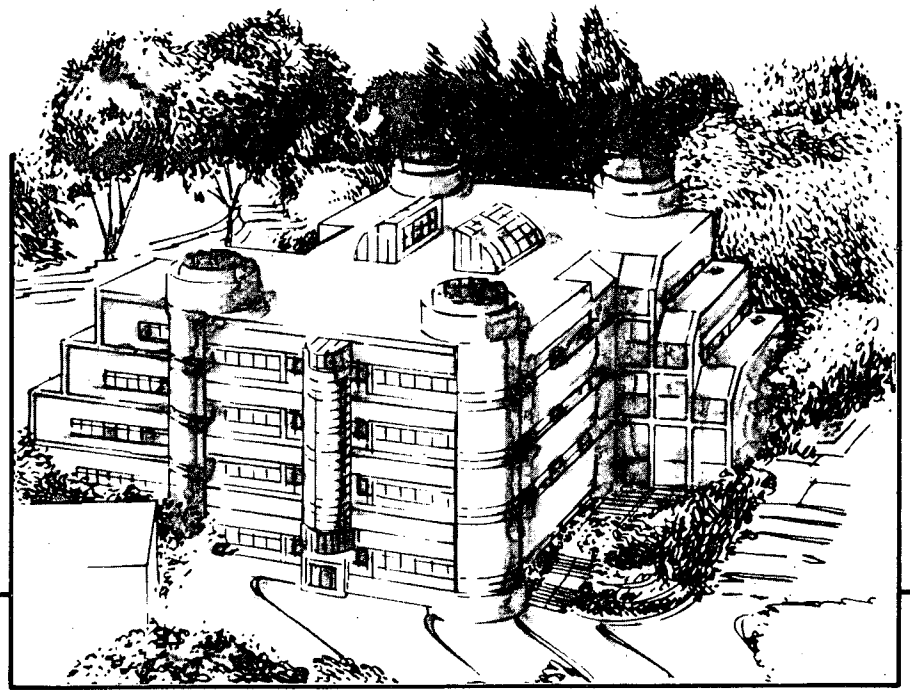
November 1990



Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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M.P. Delplancke, J.M. Powers, G.J. Vandentop,
M. Salmeron and G.A. Somorjai

Materials Science Division
Center for Advanced Materials
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720 U.S.A.

and

Department of Chemistry
University of California
Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division, U.S. Department of Energy under contract No. DE-AC03--76SF00098.

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M.P. Delplancke* , J.M. Powers, G.J. Vandentop**, M. Salmeron
and G.A. Somorjai

Center for Advanced Materials
Materials and Chemical Scienes Division
Lawrence Berkeley Laboratory
Cyclotron Road
Berkeley, CA 94720
and
Department of Chemistry
University of California
Berkeley, CA 94720

Abstract

Silicon carbide films were deposited by plasma enhanced chemical vapor deposition (PECVD) utilizing monomethylsilane (CH_3SiH_3). Silicon (100) and polycrystalline gold were used as substrates. A mass spectrometric analysis of the monomethylsilane plasma showed that the majority of the Si-C bonds were preserved in the gas phase. The composition, the density and morphology of the amorphous SiC : H (a : SiC : H) films were studied as a function of substrate temperature, composition of the ion flux bombarding the surface and the kinetic energy of these ions. The surface science techniques utilized for these investigations include XPS, AES, SEM , FTIR and Raman spectroscopies.

* on leave of absence from Universite Libre de Bruxelles, Service Metallurgie-Electrochimie, Belgium.
** present address : Intel Corporation AL3-60, 5200 NE Elam Young Parkway, Hillsboro, OR 97124-6497

I. Introduction

Silicon carbide has many favorable physical and chemical properties such as hardness and high chemical stability. Its large band gap and the possibility to dope it n-or p-type permit its electronic applications in harsh environments.

This technological potential has resulted in the development of several fabrication routes of SiC (1,2). Chemical vapor deposition techniques (CVD) usually require high temperatures (T > 1270K) that limit their area of applications. A more promising SiC preparation method at low temperature is a plasma enhanced chemical vapor deposition process (3,4). The identification and control of the parameters that determine the growth process and the physical and chemical properties of the deposits are necessary if the films are to be used in various applications.Deposition of SiC by glow discharge (plasma) has generally used SiH_4 / hydrocarbon (5) and SiH_4 / hydrocarbon/noble gas mixtures as feedstocks (6). To our knowledge, few other silicon compounds have been used in these types of experiments. Tetramethylsilane and monomethylsilane are the most common, but they were mixed with silane and regarded as the carbon source rather than the source of silicon and carbon.

In contrast with previous approaches, this paper deals with the synthesis of silicon carbide films by plasma enhanced chemical vapor deposition (PECVD) from a pure monomethylsilane feedstock gas. The purpose of this study is to characterize both the CH_3SiH_3 plasma and the physical and chemical properties of the films as a function of the deposition parameters. The properties of a : SiC : H films such as density, composition, stress, hydrogen incorporation and structure, were investigated. Comparison between films produced on an r.f. powered electrode and on a grounded (non-powered) electrode at various substrate temperatures are presented.

II. Experimental procedure.

The SiC deposition experiments were performed in the reaction chamber described in detail elsewhere (7). The schematic diagram of this system is shown in figure 1. The films were deposited on the lower electrode which could be resistively heated as high as 773 K, even when powered. Monomethylsilane gas (Huls Petrarch System 97%) was introduced via an orifice in the center of the upper electrode and was removed by a rotary and a sorption pump. For the mass analysis of the plasma species, the plasma chamber was connected through a differentially pumped middle

stage to a high vacuum chamber in which was installed a UTI 100C mass analyser. Two modes of mass spectra acquisition were used. Both neutral and positive ion species were detected when the mass spectrometer ionizer was on. Positive ions alone were detected in the ionizer-off operation mode.The contribution of the ions to the total (ions and neutral) signal was so small that it could be neglected.

Single crystal Si (100) wafers and gold foils were used as substrates. The wafers were etched in 49% HF immediately before being attached to the electrodes. The gold foils were polished with 0.05 µm alumina paste and rinse with acetone and methanol. Once in the deposition chamber, the substrate surfaces were further cleaned by argon ion bombardment, followed by the ignition of the CH_3SiH_3 plasma.

The crystalline structure of the films was examined with a Siemens diffractometer. X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Scanning Electron Microscopy were used to determine the surface composition and the morphology.The instruments utilized were a PHI 5300 ESCA system and a PHI 660 Scanning Auger Multiprobe. Argon depth profiling was performed in the XPS and AES apparatus with an eroded area of 1 cm^2 and 1 mm^2, respectively. The concentrations quoted in the following sections were thus representative of the bulk composition. Fourier Transformed Infra-Red Spectroscopy (FTIR) spectra were obtained on a Nicolet FTIR spectrometer operating in its transmission mode. The Raman analysis was performed with an Ar^+ laser operating at 488nm with a spectrometer equipped with a photon counting imaging photomultiplier tube. The thickness of the deposits was measured by a Clevite Surfanalyser 150 profilometer for films thicker than 200nm or by ellipsometry for films thinner than 200nm. Profilometry also allowed the estimation of the degree of bending of the silicon substrate induced by the stress in the deposited films. The density of the films was deduced from their mass and volume.

III. Results.

A) Composition of a CH_3SiH_3 plasma

i) Neutral species

The influence of two factors on the plasma composition was examined : the total pressure of CH_3SiH_3 and the r.f. power applied. Under all conditions, we observed four groups of peaks (fig.2). The first one was related to species containing the Si-C bond : $CSiH_z$ ($1 \leq z \leq 6$). The second and third groups could be attributed respectively

to SiH_y ($1 \leq y \leq 4$) and CH_x ($1 \leq x \leq 4$) species. The last group consisted of molecular and atomic hydrogen. The main peak appeared at 44 amu and corresponded to a monomethylsilane molecule deficient in two hydrogen atoms. Experiments with a deuterated monomethylsilane CD_3SiH_3 would allow one to unambiguously assign a structure to this 44 amu neutral fragment.

The predominance of species containing a Si-C bond in the CH_3SiH_3 plasma is a major advantage in the formation of silicon carbide films via a PECVD process. In contrast with a SiH_4 / CH_4 plasma where the majority of the Si-C bonds had to be formed at the surface of the substrate, in the CH_3SiH_3 plasma Si-C bonds were preserved in the gas phase. Therefore, the probability of obtaining Si-C bonds in the deposited films should be higher in the case of a CH_3SiH_3 plasma versus a CH_4 / SiH_4 plasma. The absence of molecular species with mass greater than 46 amu indicated a very low rate of polymerization in the gas phase. This was favorable to a nucleation on the substrates and consequently to the growth of coherent films.The gas pressure and the r.f. power supplied did not influence strongly the plasma composition. The spectra of the neutral species collected at the powered and at the grounded electrodes were very similar.

ii) ionic species

The positve ions were investigated under the same conditions of pressure and r.f. power as were the neutral species. The ions detected in the CH_3SiH_3 plasma included the following : CH_x^+ ($2 \leq x \leq 4$), SiH_y^+ ($2 \leq y \leq 4$), and $SiCH_z^+$ ($3 \leq z \leq 5$). The ions contributed 0.1% to the total flux of particles impinging the electrode surface. But the composition of the ion flux depended strongly on the electrode examined. The average degree of hydrogenation of SiH_y and $SiCH_z$ species and the number of ions containing a Si-C bond were lower at the powered electrode than at the grounded one. The difference observed in the ion flux composition at the two electrodes was attributed to the influence of the self-bias voltage that develops spontaneously at the powered electrode. The higher average electron-molecule collision energy, due to the potential drop in the vicinity of the powered electrode, results in a higher probability to break the Si-C, Si-H and C-H bonds, thus increasing the fraction of light ions.

B) Film composition

i) Influence of the substrate temperature

The deposition rate of the films grown on both electrodes decreased with increasing substrate temperature. In addition, we observed that the composition of the films deposited at the grounded electrode depended dramatically on the substrate temperature during deposition. For temperatures lower than 423K, the films deposited at the grounded electrode were heavily contaminated with oxygen (more than 10 at.%) while films deposited at 573 and 723K contained less than 1 at.% of oxygen (see table 1). The presence of oxygenated species in the films could not be attributed to the adsorption at the surface during the transfer in air from the deposition chamber into the Auger or the X-ray photoelectron spectrometer. When present, the contamination was detected in the bulk of the films as shown by argon depth profiling. All the concentrations, cited in table 1, were measured after elimination of the adsorbed layer by argon sputtering in the UHV chambers. The oxygen contamination took place during the growth process. A difference in the temperature dependance of the sticking coefficient of the oxygenated species in comparison with the sticking coefficient of Si-C species on the $Si_xC_yH_z$ growing film could explain the relationship between the contamination level and the substrate temperature. The residual gas and impurities contained in the feeding gas were probably the sources of oxygen and oxygenated fragments.

In contrast with the results obtained at the grounded electrode, the films grown at the powered electrode were only slightly contaminated even at low temperatures (table1). The presence of energetic hydrogen atoms close to the growing films at the powered electrode could result in the reduction and elimination of the oxygenated species.

AES and XPS analysis of films grown on both the powered and the grounded electrodes, indicated that they were composed of two phases (see figure 3). The first phase, characterized by a majority of Si-C bonds, was enriched in silicon in comparison with single crystal SiC analysed under the same conditions. The second phase contained mainly C-C and C-H bonds.

The powered electrode films were silicon-rich in comparison with films deposited at the grounded electrode (see table 1).The energetic hydrogen atom bombardment at the powered electrode could provoke the preferential removal of C atoms from the growing films as CH_4, with the silicon fragments being more likely to remain at the surface (3).

Hydrogen was present in the films but its concentration could not be determine by AES and XPS.

ii) Influence of the r.f. power.

Films formed at the powered electrode at 573K at three different r.f. powers (50, 75 and 100W) were investigated. The self-bias developed by the powered electrode in these conditions varied between 225V at 50W and 300V at 100W.

An increase in the deposition rate with an increasing power was observed. This was expected because the increase of the power increased the degree of dissociation of the gas.

No strong dependance of the film composition on the r.f. power was detected. The compositional variations were within the error range of AES and XPS quantitative analysis. The change in the energy of ions bombarding the growing film did not influence dramatically the ratio of carbon and silicon in the resulting film.

C) Density and stress

At both electrodes, an increase in the substrate temperature resulted in an increase in the film density. The comparison between the results obtained at the powered and the grounded electrodes at the same temperature showed that the ion bombardment also increased the density of the films. The density measured for a film deposited at 573K at the powered electrode was close to the density of bulk silicon carbide : 3.21g/cm^3 for SiC. The relevant results are presented in table 2.

The profilometer was used to estimate the degree of bending of the silicon an gold substrates induced by the stress in the deposited films. On gold and silicon the stresses observed were always compressive. At 333K at the grounded electrode, no stress was detected on the two substrates. At 573K at the same electrode a slight bending of the silicon wafer and of the gold foil was measured. The stresses in the films formed at the powered electrode were so large that the gold foils were macroscopically bent and thick films (> 1 µm) deposited on silicon wafers delaminated to release the interfacial tension. Thinner films remained attached to the silicon substrates.The adhesion of these films to the substrates, in presence of high stresses, suggested the formation of strong chemical bonds at the interfaces. The nature of

these bonds would be C-Si and Si-Si for silicon substrates and Si-Au for gold substrates.

The hardness of the films could not be measured with a microindenter because on one hand the films were too thin to avoid the influence of the substrate and on the other hand the stresses present in thicker films induced their delamination from the substrate.

D) Structure

In order to obtain information concerning the film structure, thick films (≥ 1 μm) deposited on silicon and sapphire were prepared.

X-ray diffraction analysis indicated an amorphous structure for films grown at both electrodes at all substrate temperatures (333, 423, 573 and 723K) .

The absence of any feature in the Raman spectra of the films indicated a disordered structure. These results suggested a polymer-like structure for the deposited films.

FTIR spectroscopy gave information concerning the bonding between the three major constituting elements : Si, C and H. Silicon substrates were used to observe the 250-2300 cm^{-1} region and sapphire substrates for the 2300-4000 cm^{-1} range. Sapphire was chosen for its transparency in this range of IR frequencies. Typical spectra are presented in figure 4. The spectra exhibited three main regions : one located at about 2080cm^{-1}, an other between 400 and 1100 cm^{-1}, and the last one between 2700 and 3100 cm^{-1}. Based on the works of Wieder (5) and Catherine (6), the 2080 cm^{-1} absorption band was assigned to the Si-H vibrational stretch when one, two or three carbon atoms are attached to the silicon. The presence of $-SiH_2$ group would result in a shift and a distortion of this band. The assignment of the IR absorption bands in the range 400-1100 cm^{-1} range is summarized in table 3. The stretching modes of C-H bonds in $-CH_3$ and $-CH_2$ groups are responsible for the absorption bands located in the vicinity of 3000 cm^{-1}. Figure 4 shows the comparison between the two electrodes at two temperatures 333 and 573K.

The spectrum obtained for a film deposited at the grounded electrode at 333K (fig.4a) presented features resulting from the contamination by oxygen and was not characteristic of Si-Si, Si-C, Si-H or C-H vibration modes.

An increase of temperature transformed the spectrum drastically (fig.4b). The absorption bands, of a film deposited at 573K at the grounded electrode, were

exclusively due to the vibration modes of a : SiC : H compound. The ion bombardment, at the powered electrode, induced the same modifications of the spectra (fig.4c). A close look at figure 4b and c showed that the spectra of films obtained at 573K at the grounded electrode and those of films formed at the powered electrode at 333K were very similar. The strong assymetry of the absorption band around 780 cm^{-1} reflected the presence of SiH_2 groups (≈ 620 cm^{-1}) and of $Si-CH_3$, $Si-CH_2$ groups (shoulder at ≈1000 cm^{-1}). This was confirmed by the absorption bands presented in the region 1250-1400 cm^{-1} corresponding to bending modes of CH_2-Si (1250 cm^{-1}), CH_3-Si (1350 cm^{-1}) and CH_3-SiH_3 (1400 cm^{-1}). The stretching modes of CH_2 and CH_3 groups are unresolved but the assymetry of the peak indicated a higher proportion of CH_2 groups. As shown by the relative intensity of the Si-H stretching band, the temperature influence on the hydrogen incorporation was stronger than the effect of the ion bombardment.

Films deposited on the powered electrode at high temperature (573K) combined the effects, on the hydrogen content, of both the ion bombardment and the temperature. In comparison with the spectra discussed in the previous paragraph, those films formed at the powered electrode at 573K presented less features (see figure 4d). The absence or the lower intensity of certain absorption bands were always related to a smaller degree of hydrogen incorporation. The intensity of the Si-H stretching mode (2080 cm^{-1}) was reduced by a factor of two between the powered and the grounded electrode. The CH_3-Si bending modes were absent. The combination of a high substrate temperature and of an energetic ion bombardment increased the number of Si-C bonds by reducing the hydrogen concentration in the film. This observation was in agreement with the high density (3.2 g/cm^3) observed for films prepared at 573K on the powered electrode.

IV. Conclusions.

Deposition of a : SiC : H films by PECVD from CH_3SiH_3 on gold and silicon substrates was investigated. The characteristics of the films, including composition, structure, density and IR absorption bands, were determined as a function of the deposition variables, including plasma composition, substrate temperature, r.f. power and ion flux.

Raman spectroscopy and X-ray diffraction measurements suggested a polymer-like structure of the films prepared by PECVD from a pure monomethylsilane feed-stock.

It was observed that films formed at the powered electrode at high temperature (573K) exhibited superior properties compared with films formed at the grounded electrode under the same conditions. The density of the powered electrode films formed at 573K was high (3.2 g/cm^3) and close to the bulk value. A large amount of compressive stress was developed in these films, but their adhesion to the substrates (gold or silicon) suggested the formation of strong chemical bonds at the interfaces.

The differences between the powered and the grounded electrode films could be attributed to the energetic ion flux bombarding the surface of the powered electrode. This bombardment was responsible for the lower hydrogen incorporation, for the purity of the films grown at this electrode, and for the possible formation of interfacial bonds.

The substrate temperature also controlled the properties of the films. Its increase reduced the hydrogen concentration as well as the oxygen contamination.

The mass spectrometric analysis of CH_3SiH_3 plasma showed clearly the advantage of this gas in the preparation of SiC. The majority of the Si-C bonds were preserved in the gas phase , increasing the probability to include this type of bonds in the films. Differences in the ion flux composition were observed between the two electrodes and could explain the difference in the film composition.

Optical and mechanical properties of the films are presently under investigation.

Acknowledgements.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under contract No DE-AC03-76SF00098.

The authors would like to thank Michael Rubin for use of the FTIR spectrometer and Joel Ager for the Raman spectroscopy analysis.

M.P. Delplancke would like to acknowledge the financial support by NATO and by the Fulbright program.

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	GROUNDED ELECTRODE				POWERED ELECTRODE			
T (K)	Si 2p BE (eV)	C 1s BE (eV)	concentrations		Si 2p BE (eV)	C 1s BE (eV)	concentrations	
			Si / C	O (at.%)			Si / C	O (at.%)
333	98.5 102.0	284.6 280.7		15	100.0	284.8 283.2	1.5	< 1
423	99.9	284.7 283.0	1.1	10	100.0	284.6 283.1	1.9	< 1
573	100.1	284.8 283.3	1.3	< 1	100.2	284.6 283.2	1.9	< 1
723	100.1	284.6 283.1	1.7	< 1	100.1	284.7 282.9	2.3	< 1

Table 1 : XPS analysis of films deposited on gold foils.
r.f. power = 50 W, CH_3SiH_3 pressure = 13.3 Pa
Si 2p BE = Si 2p binding energy obtained by curve fitting
C 1s BE = C 1s binding energy obtained by curve fitting

T (K)	GROUNDED ELECTRODE		POWERED ELECTRODE	
	Deposition rate (nm/min)	Density (g/cm^3)	Deposition rate (nm/min)	Density (g/cm^3)
333	32	1.5	27	2.0
573	18	2.0	15	3.2

Table 2 : Deposition rate and density of the films as a function of the substrate temperature.
Density of single crystal SiC : 3.21 g/cm^3.

wavenumber (cm^{-1})	vibration mode
620	Si-H, $Si-H_2$ wagging and rocking
675-680	Si-C stretching
780	Si-C stretching
	$Si-CH_3$ rocking or wagging
860	$Si-H_2$, $(SiH_2)_n$ bending
980-990	$Si-CH_3$ rocking
1020-1040	$Si-CH_2$ rocking or twisting

Table 3 : Assignment of the IR absorption bands in the 400-1100 cm^{-1} range. From reference 7

Figure captions

figure 1 : Schematic diagram of the PECVD system.

figure 2 : Mass spectrum of the neutral species collected at the grounded electrode
CH_3SiH_3 pressure = 15.7 Pa, r.f. power = 100 W

figure 3 : Film deposited at 723K at the powered electrode on gold.
CH_3SiH_3 pressure = 13.3 Pa, r.f. power = 50W
a) C 1s photoelectron line
b) Si 2p photoelectron line

figure 4 : FTIR spectra
a) film deposited at the grounded electrode at 333 K
b) film deposited at the grounded electrode at 573 K
c) film deposited at the powered electrode at 333 K
d) film deposited at the powered electrode at 573 K
CH_3SiH_3 pressure = 13.3 Pa, r.f. power = 50 W.

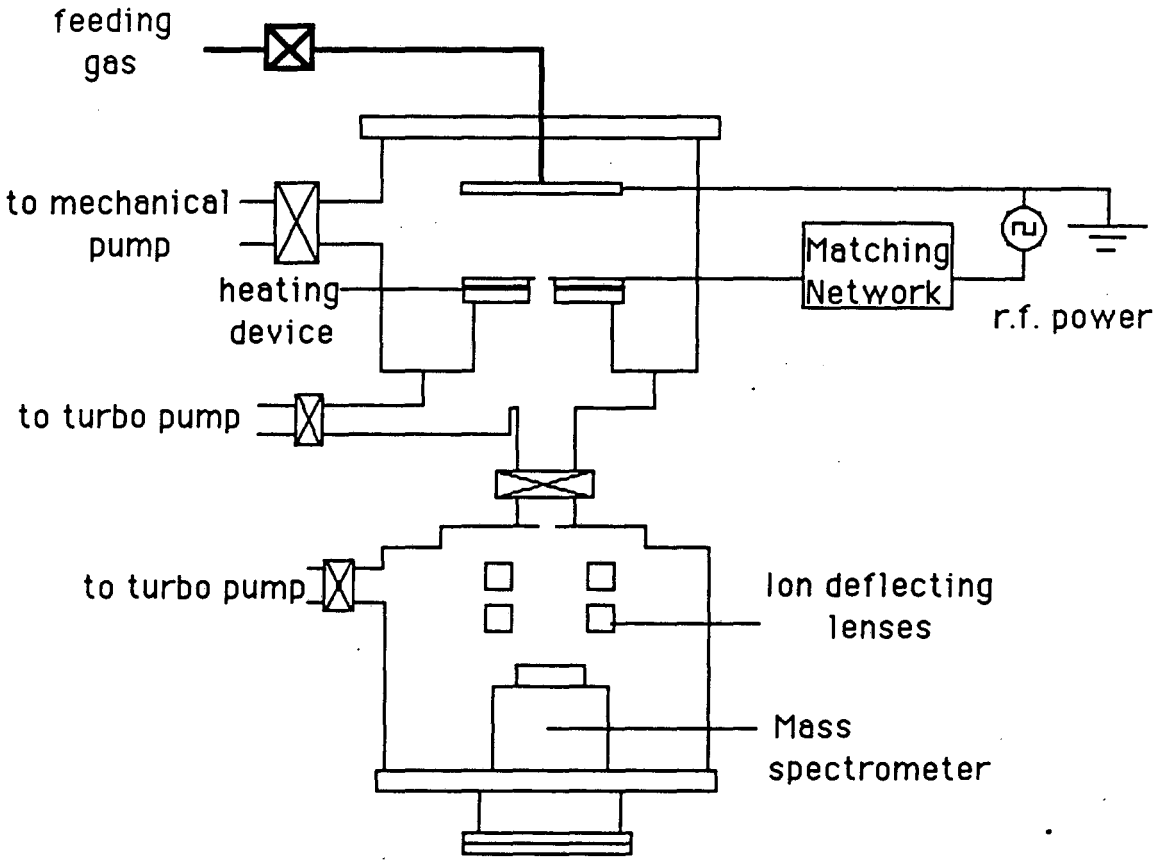

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Fig. 1

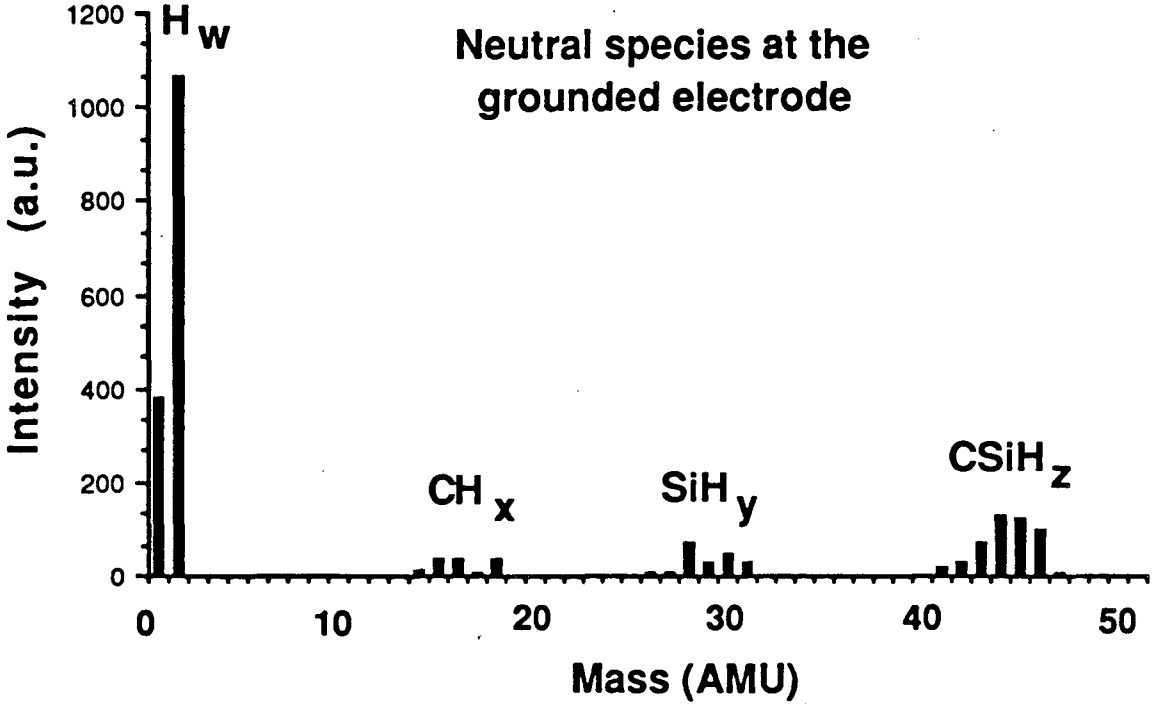

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Fig. 2

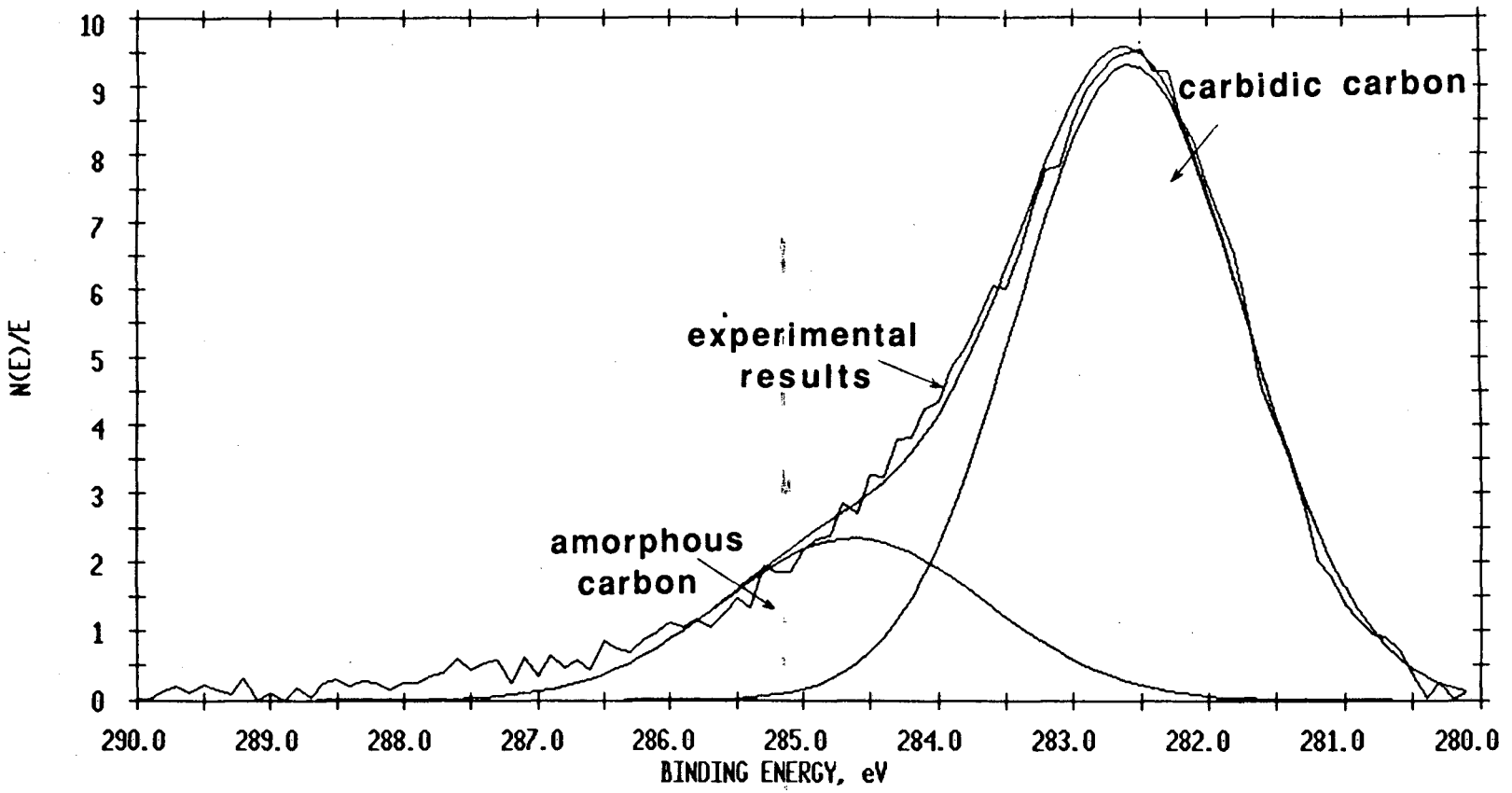

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Fig. 3a

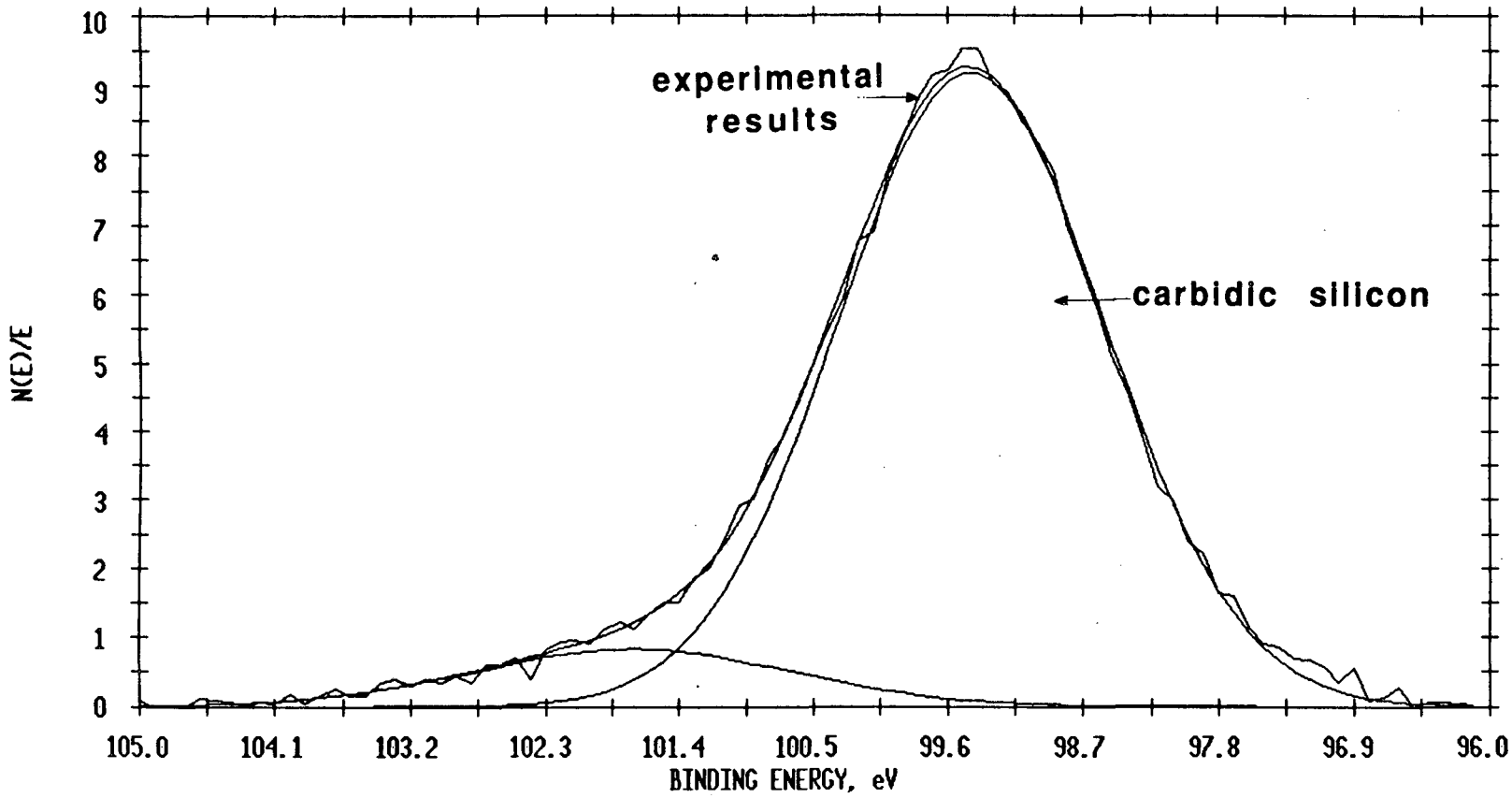

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Fig. 3b

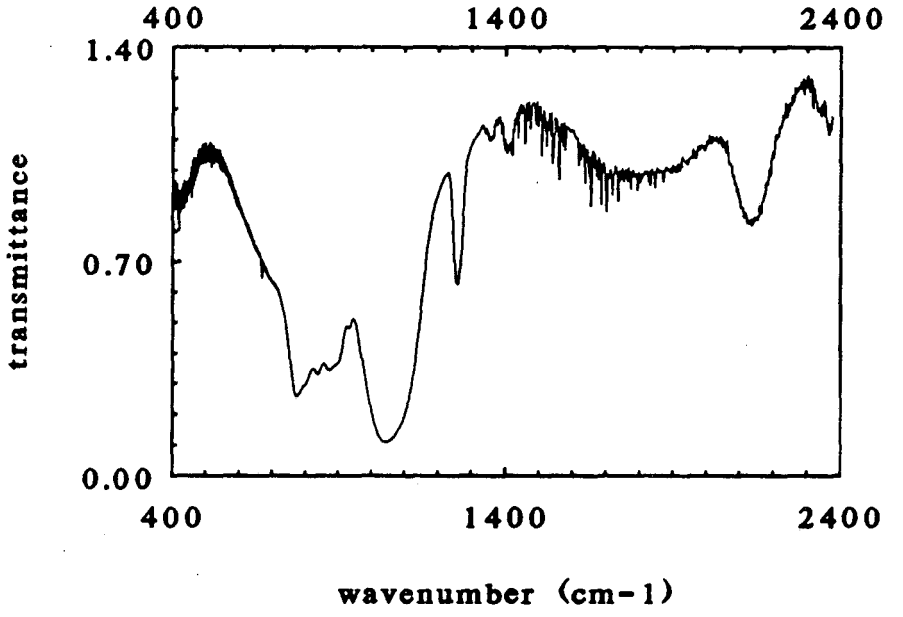

Fig. 4a

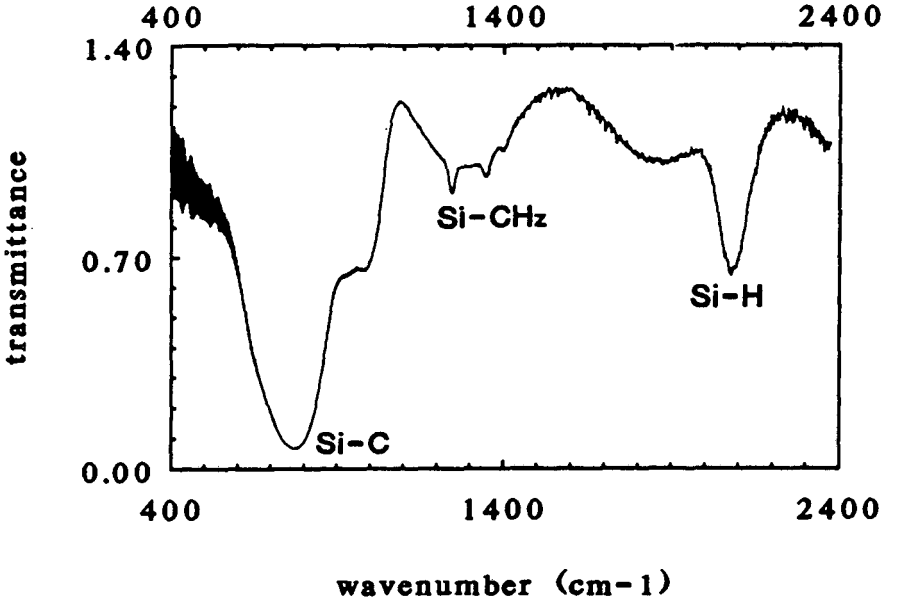

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Fig. 4b

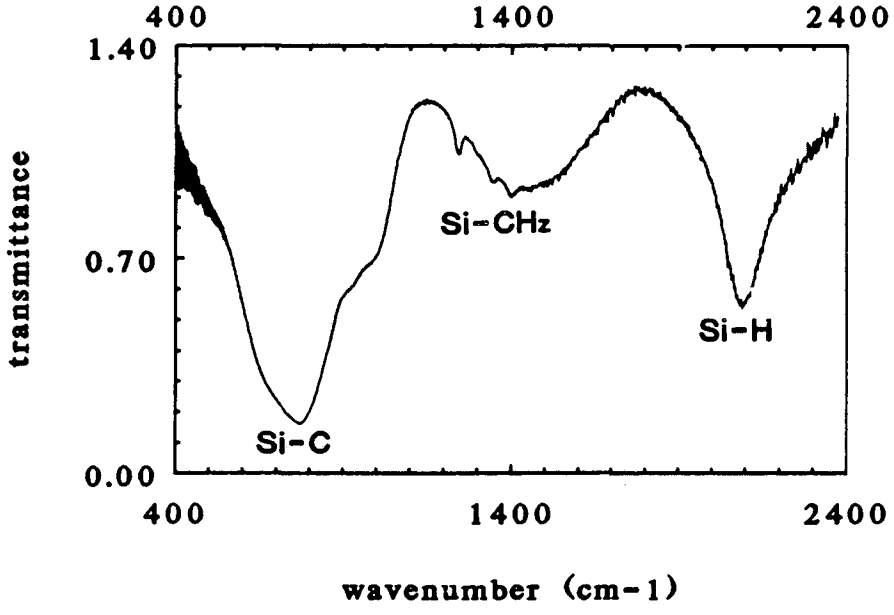

Fig. 4c

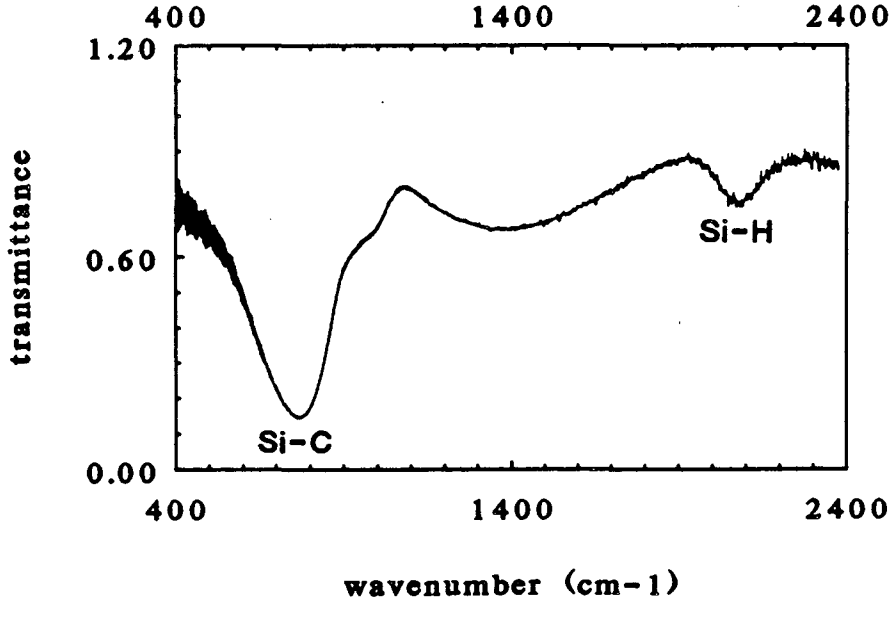

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Fig. 4d

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