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TECHNICAL REPORT NO. 64

FTIR Studies of CH₃OH on Porous Silicon

by

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Submitted To

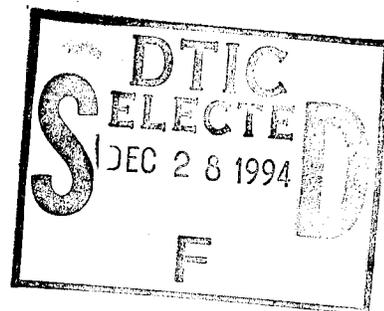
Materials Research Society Symposium Proceeding

Surface Science Center
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Fall November 1994

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19941223 011

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REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

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| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE Fall (Nov.) 1994 | 3. REPORT TYPE AND DATES COVERED Preprint |
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|---|--------------------|
| 4. TITLE AND SUBTITLE FTIR Studies of CH ₃ OH On Porous Silicon | 5. FUNDING NUMBERS |
|---|--------------------|

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| 6. AUTHOR(S) John A. Glass, Jr., Edward A. Wovchko, and John T. Yates, Jr. | |
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| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Surface Science Center Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260 | 8. PERFORMING ORGANIZATION REPORT NUMBER |
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| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Division, Code 313 800 North Quincy Street Arlington, Virginia 22217-5000 | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER |
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| 11. SUPPLEMENTARY NOTES |
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| 12a. DISTRIBUTION / AVAILABILITY STATEMENT | 12b. DISTRIBUTION CODE |
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| 13. ABSTRACT (Maximum 200 words) <p style="text-align: center;">Fourier transform infrared spectroscopy (FTIR) was used to investigate the reaction of methanol with porous silicon and hydrogen passivated porous silicon. At 300 K methanol adsorbs onto hydrogen free porous silicon by cleavage of the O-H bond. Both of the resulting surface species, Si-H and Si-OCH₃, were determined to be stable up to ~500 K. Above 500 K the Si-OCH₃ moiety decomposes by breakage of the C-O and C-H bonds. The resulting carbon and oxygen were incorporated into the porous layer and additional Si-H surface species were detected. Further heating to 900 K removed the Si-H surface species. Adsorption of methanol onto hydrogen-passivated porous silicon did not occur until 600 K. At temperatures beyond 600 K, oxygen and carbon incorporation into the porous layer and Si-OCH₃, Si-CH₃, and Si-H surface species were seen. The previously unseen Si-CH₃ surface species is believed to be stabilized by oxygen incorporation.</p> |
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| 14. SUBJECT TERMS Silicon Hydrogen Porous Silicon Methyl Alcohol Methyl | 15. NUMBER OF PAGES 6 |
| | 16. PRICE CODE |

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| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---------------------------------------|--|---|----------------------------|

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ABSTRACT

Fourier transform infrared spectroscopy (FTIR) was used to investigate the reaction of methanol with porous silicon and hydrogen passivated porous silicon. At 300 K methanol adsorbs onto hydrogen free porous silicon by cleavage of the O-H bond. Both of the resulting surface species, Si-H and Si-OCH₃, were determined to be stable up to ~500 K. Above 500 K the Si-OCH₃ moiety decomposes by breakage of the C-O and C-H bonds. The resulting carbon and oxygen were incorporated into the porous layer and additional Si-H surface species were detected. Further heating to 900 K removed the Si-H surface species. Adsorption of methanol onto hydrogen-passivated porous silicon did not occur until 600 K. At temperatures beyond 600 K, oxygen and carbon incorporation into the porous layer and Si-OCH₃, Si-CH₃, and Si-H surface species were seen. The previously unseen Si-CH₃ surface species is believed to be stabilized by oxygen incorporation.

INTRODUCTION

Two important technologies - electronic device fabrication and catalytic silane and siloxane production [1-3] - use silicon and silicon containing materials. It is surprising that the surface reaction chemistry of organic and aqueous solvents with both silicon (100) crystals and amorphous silicon has not been more widely studied.

Clearly, interactions between solvents employed in the cleaning, production, and growth protocols, and silicon (100) surfaces [4, 5] will become more critical with increasing demand for more efficient removal of contaminants. Initial studies of H₂O on Si(100) have given insights into the dissociative adsorption of H₂O and resulting surface species [6, 7]. Organic solvent decomposition on Si(100), however, has only just recently begun to receive attention [8, 9].

Research on silicon optoelectronics has focused primarily on porous silicon and its photoluminescence properties. However, the cause of the photoluminescent process has been the subject of much debate [10, 11]. This technology would probably involve solvent use on porous silicon.

The Direct Synthesis of silane and siloxanes has recently begun to be studied [3, 12]. The overall goal in these studies has been to determine the mechanistic aspects of the process. The reaction of organic molecules, such as methanol, with silicon is a first step in understanding this technologically important process.

Transmission Fourier Transform Infrared Spectroscopy (FTIR) is sensitive to surface species and reactions provided the material under study has a high surface area (~10¹⁸

sites / cm²). Single crystals of silicon have insufficient surface site density to apply transmission FTIR spectroscopy.

Porous silicon, a high surface area material, makes an excellent silicon surface for gathering transmission FTIR spectra from molecules adsorbed on silicon. Concerns relative to porous silicon being indicative of a crystalline sample have been previously addressed [7, 13, 14]. In addition, transmission FTIR provides a window into high pressure experiments unavailable with electron spectroscopy.

Therefore, we have studied, by transmission FTIR, the adsorption and reaction of CH₃OH with porous silicon and hydrogenated (passivated) porous silicon.

EXPERIMENTAL

The experimental preparation and the mounting of the porous layer into the vacuum infrared cell has been described elsewhere [15]. Briefly, each p-type Si(100) crystal was slotted, cleaned by the RCA procedure, etched in a 48% HF (aq) and anhydrous CH₃CH₂OH solution for 20 sec at 100 mA, and dipped into 48% HF (aq) for 15 seconds. Following these preparations the crystal was mounted in the infrared cell having base pressures ~ 10⁻⁸ Torr.

Infrared spectra were recorded on a Mattson Research Series I Fourier transform infrared spectrometer running Mattson Fourier Infrared Software Tools (FIRST). For each infrared spectrum the liquid nitrogen cooled HgCdTe detector collected 1024 scans at a spectral resolution of 2 cm⁻¹. All spectra were recorded under evacuation at 300 K. Window and crystal lattice bands were subtracted out.

Pure anhydrous CH₃OH (Baker 99.95%), and isotopically labeled CH₃OD (Merck, 99 % isotopic purity), CD₃OH (Merck, 99 % isotopic purity), and ¹³CH₃OH (Cambridge Isotopes, 99% isotopic purity) were used in this study. Each adsorption was completed by allowing 9 Torr of the desired methanol to interact with the porous silicon for 15 min. Removal of surface hydrogen and heating studies were accomplished by flash heating to 750 K prior to methanol exposure and by heating from 300 K to 900 K in 100 K increments.

RESULTS AND DISCUSSION

The porous silicon, following removal of surface hydrides at 750 K, was exposed to 9 Torr of CH₃OH at 300 K. The chemisorption of CH₃OH, Figure 1, proceeds by breakage of the O-H bond to form Si-OCH₃ and Si-H surface species. Similar behavior has been observed previously [7, 9, 16] and studies on a second porous silicon sample using CH₃OD confirmed this dissociative process. Interestingly, the Si-H frequency produced from CH₃OH is observed at 2090 cm⁻¹. This shift is either due to surface moiety interactions (OCH₃ and H) or to new surface site development after hydrogen removal from electrochemically etched silicon.

Decomposition of the Si-OCH₃ and Si-H surface species, Figure 2, resulted when the sample was heated from 300 K to 900 K. From 300 K to ~500 K both the Si-OCH₃ and the

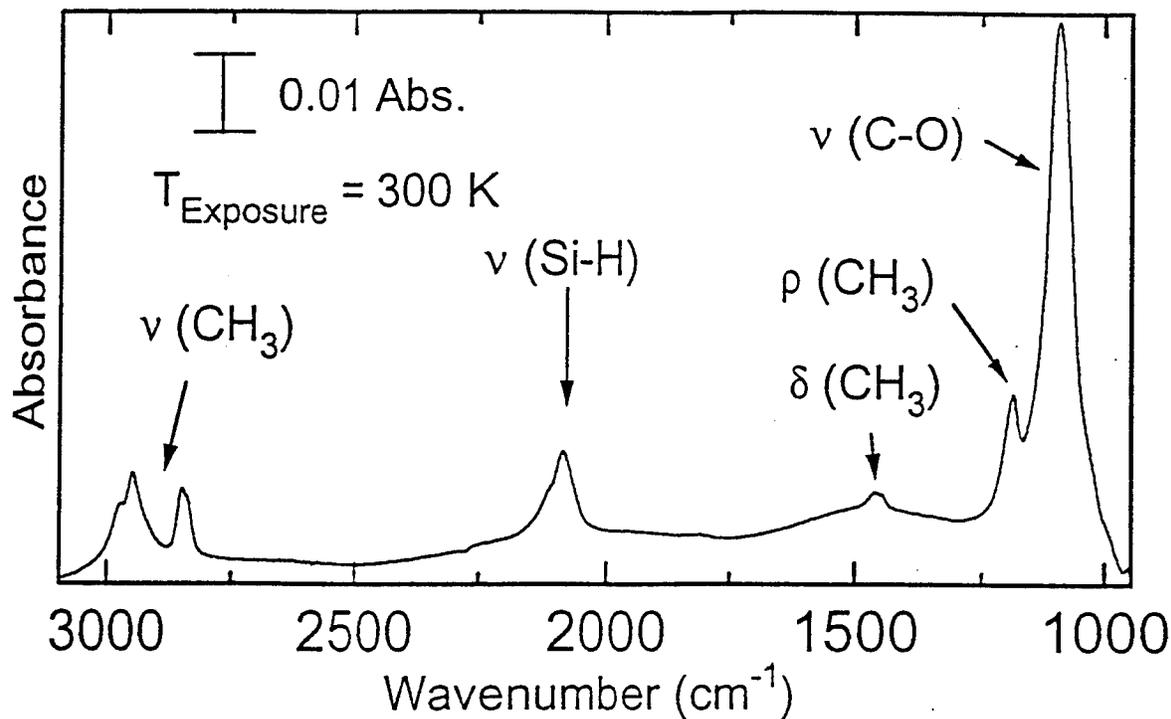


Figure 1: Adsorption of CH_3OH on Porous Silicon at 300 K.

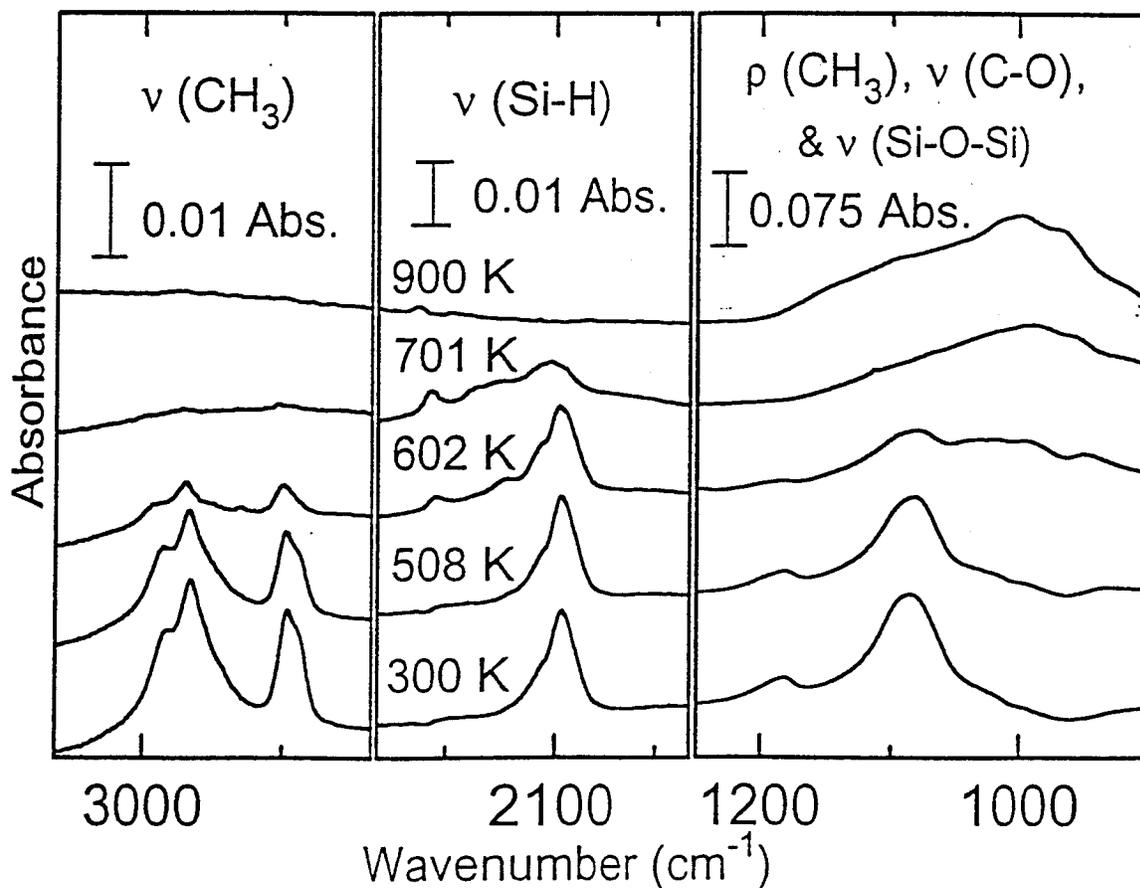


Figure 2: Annealing of CH_3OH Adsorbed on Porous Silicon.

Si-H surface species are stable. However, beyond 500 K, and up to 900 K, the $\nu(\text{OCH}_3)$ modes ($\nu(\text{CH}_3)$ modes (centered at 2946 cm^{-1}), the $\delta(\text{CH}_3)$ mode (1461 cm^{-1}), the $\rho(\text{CH}_3)$ mode (1182 cm^{-1}), and the $\nu(\text{C-O})$ mode (1086 cm^{-1})) all decrease uniformly to zero. This is consistent with previous studies in which the Si-OCH₃ surface species began to decompose at 500 K [9, 16]. In addition, an increase in the $\nu(\text{Si-O-Si})$ and $\nu(\text{Si-C})$ modes (998 cm^{-1} and 761 cm^{-1} respectively) and an increase in the $\nu(\text{Si-D})$ signal when CD₃OH is adsorbed over this same temperature range, indicates that both C-H and C-O bond breakage is occurring. In accordance with other studies of hydrogen on porous silicon [14] the $\nu(\text{Si-H})$ mode (2091 cm^{-1}) begins decreasing in intensity at $\sim 550\text{ K}$. This loss is accompanied by intensity increases corresponding to new Si-H species at 2269 cm^{-1} and 2169 cm^{-1} (Figure 2). These new Si-H species are more stable than $\nu(\text{Si-H})$ species at 2091 cm^{-1} . These species result from oxygen incorporation into the porous layer from Si-OCH₃ decomposition [7, 17]. The low frequency region of the spectrum shows three new modes developing at 500 K. These new observed bands are $\nu(\text{Si-O-Si})$ (998 cm^{-1}), $\delta(\text{O}_x\text{Si-H})$ (775 cm^{-1}), and $\nu(\text{Si-C})$ (761 cm^{-1}) [7, 17]. The $\delta(\text{O}_x\text{Si-H})$ assignment was based on our isotopic labeling studies with ¹³CH₃OH and CD₃OH. Intensity variations versus annealing temperature showed that the intensity of both $\nu(\text{Si-O-Si})$ and $\delta(\text{O}_x\text{Si-H})$ were consistent with the loss of the CH₃ modes, and the C-O mode. The $\nu(\text{Si-C})$ mode at 761 cm^{-1} , however, begins to show increased intensity only above 650 K. This latent development of the Si-C band at 761 cm^{-1} is probably due to interference from $\delta(\text{O}_x\text{Si-H})$ (775 cm^{-1}) and/or incomplete lattice mode subtraction. Finally, after heating the sample to 900 K all the OCH₃ and H surface species were removed and only the final decomposition products, yielding the $\nu(\text{Si-O-Si})$ and $\nu(\text{Si-C})$ modes, are evident.

REACTION OF PASSIVATED POROUS SILICON WITH CH₃OH

Exposure of 9 Torr of CH₃OH to the passivated (hydrogen covered) porous silicon at 300 K - 600 K resulted in no reaction, as shown in Figure 3. However, at 600 K and above, methanol reacts with the open sites generated by the loss of Si-H. Since 600 K is above the decomposition temperature of the OCH₃ surface species, the spectra show the formation of the thermal decomposition products seen previously [this work, 7, 17]. This lack of reactivity at temperatures up to 600 K is consistent with other studies which have shown a hydride layer on silicon to provide a barrier to surface reactions [18, 19]. Further high temperature reactions with CH₃OH (g) showed a new spectral feature developing at 1276 cm^{-1} and the rapid development of $\nu(\text{Si-O-Si})$ and $\nu(\text{Si-C})$ spectral features shifted to higher frequency (998 cm^{-1} to 1025 cm^{-1} and 761 cm^{-1} to 815 cm^{-1}). The feature at 1276 cm^{-1} is interpreted as a $\delta(\text{CH}_3)$ mode from a CH₃ directly bound to silicon [17, 20]. The $\nu(\text{CH}_3)$ modes from this Si-CH₃ species were indistinguishable from the $\nu(\text{CH}_3)$ modes of the Si-OCH₃ surface species. The Si-CH₃ surface species also exhibited a high degree of thermal stability (above 900 K) as compared to CH₃ adsorbed on Si(100) (decomposes at 600 K) [20]. The shifting of the $\nu(\text{Si-O-Si})$ and the $\nu(\text{Si-C})$ modes to higher frequency was due to the oxygenation of the surface from the extensive Si-OCH₃ decomposition. A similar type of behavior was observed earlier for hydrogen on an oxygenated surface [this work].

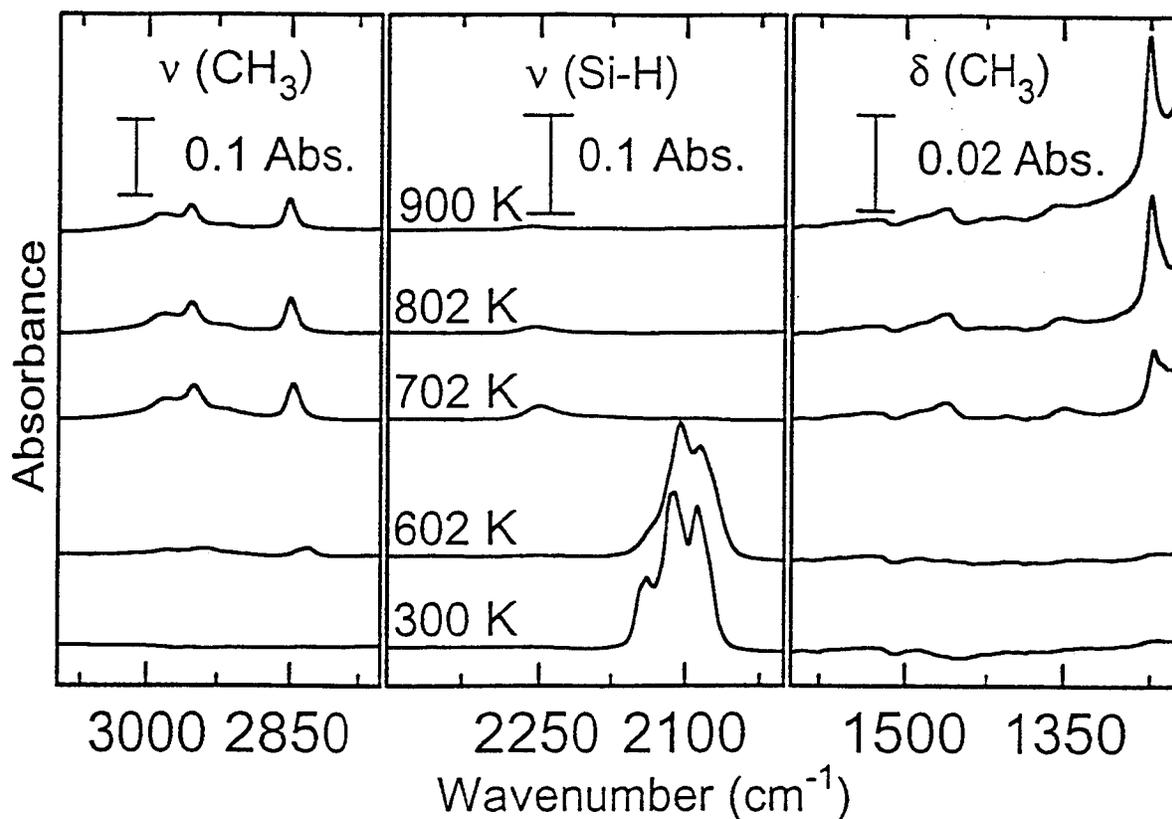


Figure 3: Reaction of CH_3OH (g) with Passivated Porous Silicon.

CONCLUSIONS

The following features for CH_3OH decomposition on porous silicon have been observed:

1. CH_3OH reacts with unpassivated porous silicon at 300 K to form Si-OCH_3 and Si-H surface species by breakage of the O-H bond.
2. Heating the Si-OCH_3 and Si-H surface species to ~ 500 K results in the decomposition of the Si-OCH_3 by both C-H and C-O bond breakage to form Si-H surface species. Subsequent oxygen (ν (Si-O-Si)) and carbon (ν (Si-C)) incorporation into the porous silicon is observed. Further heating to 900 K results in the loss the Si-H surface species.
3. Reaction of CH_3OH (g) with hydrogen-passivated porous silicon results in no reaction until 600 K.
4. Temperatures > 600 K cause CH_3OH (g) to react with the freshly formed open Si sites. The Si-OCH_3 , Si-CH_3 , and Si-H surface species and incorporated oxygen (Si-O-Si) and carbon (Si-C) species are also formed.
5. Heating of the Si-OCH_3 , Si-CH_3 , and Si-H species under CH_3OH (g) generates more intense Si-O-Si and Si-C infrared intensities and loss of the Si-H infrared intensity.
6. The stabilization of the Si-CH_3 species and the shift of ν (Si-O-Si) and ν (Si-C) modes to higher frequency is likely due to the high surface coverage of oxygen on the silicon surface.

ACKNOWLEDGMENTS

We thank the Office of Naval Research for their support of this work. We would also like to thank John C. Camp for discussions and comments.

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