Investigation of Pyrolyzed Polyimide Thin Film as MEMS Material

**Keisuke Naka*, Hideki Nagae*, Masao Ichiyanagi*,
Ok Chan Jeong**, and Satoshi Konishi*****

Abstract—**Pyrolyzed polyimide is explored in terms of MEMS material. This paper describes chemical, electrical, mechanical properties of pyrolyzed polyimide (PIX-1400) thin film as MEMS material. When polyimide thin film was pyrolyzed at 800 °C for 60 minutes in N_2 ambient, the residual ratio of pyrolyzed film thickness measured with a surface profiler is about 49 %, and the resistivity is about 2.17×10^{-2} Ωcm. From the result of the load-deflection test, the estimated Young's modulus and initial average stress of pyrolyzed polyimide are 67 GPa and 30 MPa, respectively. As one demonstration of MEMS structures of pyrolyzed polyimide, the fabrication method of the microbridge structure is proposed for a micro heater and a resonator.**

Index Terms—**Pyrolyzed polyimide, Carbon, MEMS, Chemical Stability, Electrical property, Mechanical properties**

I. INTRODUCTION

Carbon materials have many applications due to their outstanding electrical, mechanical, thermal, and chemical properties. For example, the graphite is used as electrode for arc-discharge and porous carbons are also attractive as absorbent materials in technologies related to pollution control. Generally, carbon materials are prepared by the pyrolysis of various carbonaceous precursors such as wood, coal, lignite and so on. Polymers can also be used as precursors of carbon materials. Carbon materials derived from various polymers are called pyrolyzed polymer. There are many reports of pyrolyzed polymers through experimental results of conductivity and XPS analysis [1-3]. According to Ref. [4], the pyrolyzed polymer derived KAPTON film was obtained 100 S / cm conductivity at 900 °C pyrolysis temperature.

Micromachining technology will allow us to fabricate various structures of polymers. The fabricated structures can be transformed into pyrolyzed polymers so as to obtain fine pyrolyzed polymer structures. Appling pyrolyzed polymers to MEMS require further exploring of properties of pyrolyzed polymers. Mechanical properties as well as electrical properties become important for materials of MEMS. In addition, it is also very important to provide the pyrolyzed polymers under less than 1000 °C by taking into consideration of compatibility with pyrolysis process and MEMS fabrication process. Recently, S. Ranganathan et al. reported photoresist-derived carbon for MEMS and electrochemical applications [5]. S. Konishi et al. reported parylene-pyrolyzed carbon for MEMS application [6].

In this paper, polyimide is investigated as a precursor of the pyrolyzed polymer. Polyimide films have been used in MEMS structures and a sacrificial layer [7-8]. Pyrolyzed polyimide for MEMS application is explored and discussed through various kinds of test such as chemical stability, electrical property and mechanical properties.

Manuscript received January 15, 2005; revised March 15, 2005

*The Graduate School of Science and Engineering, Ritsumeikan University
**Center of Promotion of the COE program, Ritsumeikan University
***Department of Micro System Tech., Faculty of Science and Engineering, Ritsumeikan University
1-1-1 Noji-higashi Kusatsu Shiga, 525-8577 JAPAN
E-mail: konishi@se.ritsumei.ac.jp

II. CHARACTERIZATION OF PYROLYZED POLYIMIDE IN MEMS

In this paper, for the pyrolysis process of polyimide, PIX-1400 (HD MicroSystems, JAPAN) was used. After spin coating process of PIX-1400, the polyimide film on silicon substrate with silicon nitride was baked at 350 °C for 60 minutes in an oven. The prepared samples were ramped heat up at 10 °C / min to the maximum temperature, maintained for 60 minutes, and cooled down at 2.0 °C / min in N_2 ambient. For the basic understanding of pyrolysis temperature to polyimide, the thermal gravimetric analysis (TGA , 10 °C/min ramp rate from 20 to 1000 °C, N_2 ambient) was used for the observation of weight loss. The weight was drastically reduced around 600 °C.

1. Thickness Change

The drastic shrinkage is caused in pyrolyzed polymers due to changes in their chemical compositions. The thickness variation of polyimide before and after pyrolysis was measured with a surface profiler (Alpha-Step500, KLA Tencor). For sample fabrication, polyimide was spun at 4000 rpm on silicon substrate with silicon nitride and baked. After baking, the measured thickness of polyimide was 1.3 µm. Next, polyimide was patterned into square pattern with O_2 plasma etching process at 6 minutes. Finally, samples were pyrolyzed at various temperatures.

Fig. 1 shows the change of thickness of polyimide depending on pyrolysis temperature. The thickness of polyimide was determined from the height differences between the polyimide and the substrate. Change of thickness stands for a ratio of the thickness of the pyrolyzed polyimide to the initial thickness of polyimide. The test results are divided into three major phases as shown Fig. 1. The ratio of the residual ratio to pyrolysis temperature [% / °C] in phase II is 5 times faster than one in phase I. Above 700 °C, the shrinkage ratio is gradually affected by pyrolysis temperature and its speed is 0.33 times slower than phase II. The main degradation occurred below 700 °C as suggested from TGA observation. The change of thickness of the pyrolyzed polyimide amounted to 45.3 % at 900 °C pyrolysis temperature.

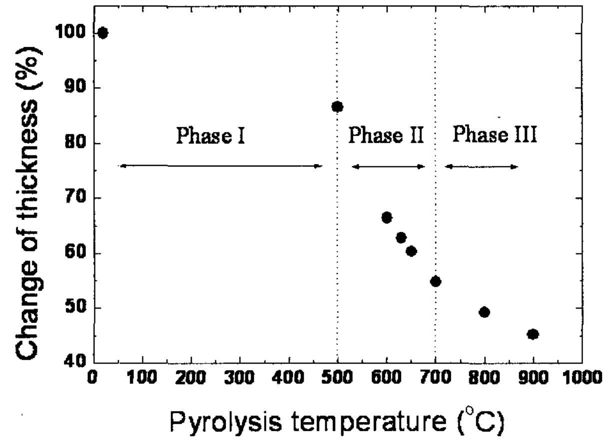


Fig. 1. Change of the film thickness after pyrolysis process

2. Chemical Stability

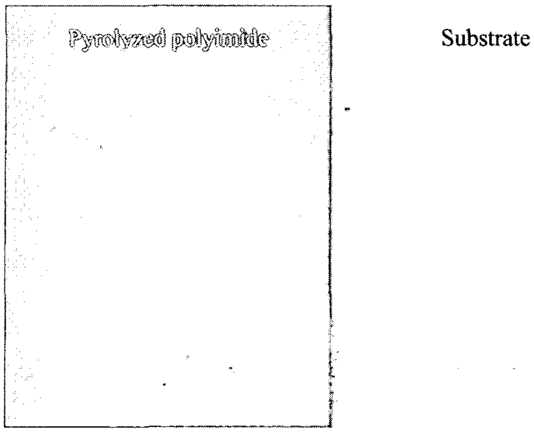
Chemical stability of pyrolyzed polymers is one of the important issues for process design of devices using pyrolyzed polymers. In the investigation of chemical stability of pyrolyzed polyimide, 1.3 µm thick polyimide on a silicon substrate with silicon nitride were used. The pyrolysis temperature was from 600 °C to 800 °C. The pyrolyzed samples were dipping into various etchants and acids used in MEMS fabrication process for a certain time. The change of the thickness was measured with the surface profiler.

Table 1 shows the summarized test result of chemical

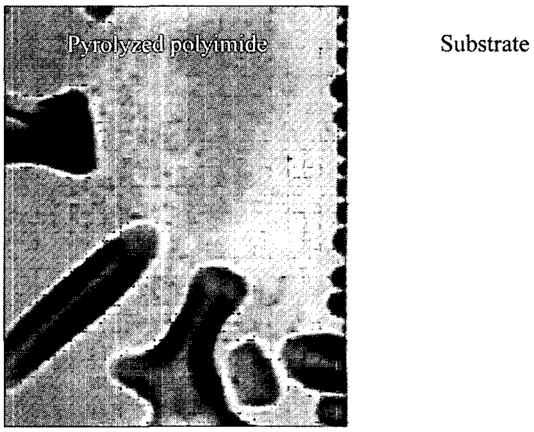
Table. 1. Summarized chemical stabilities of pyrolyzed polyimide against various metal etchants, acids and etc. used in MEMS fabrication process

Etchant or acid	at 600°C	at 700°C	at 800°C
Al etchant (H_3PO_4+HNO_3+CH_3COOH)	○	○	○
Au etchant (I_2 + KI)	○	○	○
Cr etchant ($Ce(SO_4)_2 \bullet (NH_4)_2 SO_4 2H_2O + HClO_4$)	○	○	○
$NH_4F \bullet HF$ 14%	×	△	△
Sulfuric acid	○	○	○
Hydrochloric acid	○	○	○
Sulfuric acid + hydrogen peroxide solution	○	○	○
TMAH 2.38%	○	○	○
KOH 17 wt% solution	×	×	×
Acetone	○	○	○
Ethanol	○	○	○

○ : No changed, △ : Peel off after 24 hours, × : Peel off immediately.



(a) No serious change



(b) Peeled film

Fig. 2. Photographs of pyrolyzed polyimide thin films after investigation of chemical stability.

stability. When the sample was kept into most of etchants and acids, there was no serious change in films as shown Fig. 2 (a). When the sample was kept into Chromium etchant for 24 hours, pyrolyzed polyimide was peeled off as shown Fig. 2 (b). In the case of BHF and KOH, pyrolyzed polyimide was peeled off immediately. Considering the normal chemical and wet etch-process time in MEMS, pyrolyzed polyimide has a tolerance to most of etchants and acids using MEMS fabrication process.

3. Electrical Property

In this paper, resistivity of pyrolyzed polyimide is evaluated for electrical property of pyrolyzed polyimide. For investigation of electrical property, Cr / Au (40 Å / 1100 Å) were evaporated on silicon substrate with silicon nitride, and then patterned. Polyimide was spun at 4000 rpm and baked. After baking, the measured thickness of polyimide was 1.3 μm. Next, polyimide was patterned into square pattern by O_2 plasma at 6 minutes. Finally, sample was pyrolyzed at various temperatures. Fig. 3 shows the photograph of the sample for electrical property evaluation.

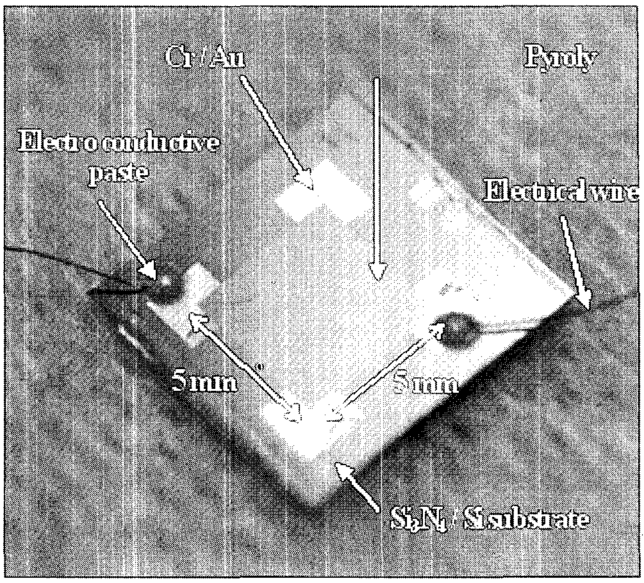


Fig. 3. Photograph of the fabricated pyrolyzed polyimide for electrical property evaluation

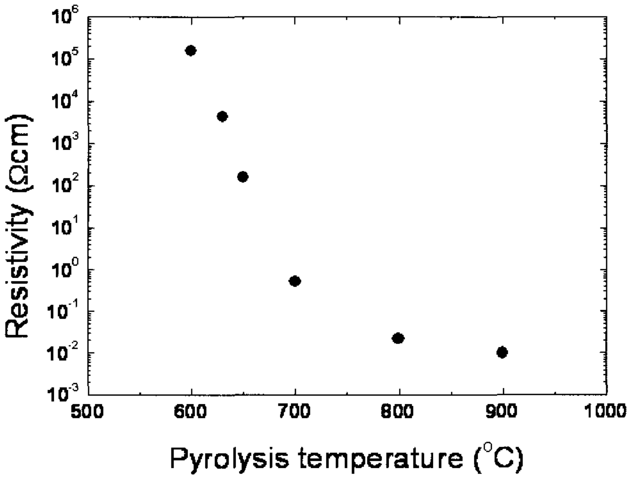


Fig. 4. Measured resistivity of pyrolyzed polyimide

Fig. 4 shows the resistivity of the pyrolyzed polyimide depending on pyrolysis temperature. The resistivity was calculated from the measured sheet resistance and the thickness of pyrolyzed polyimide. Above 600 °C pyrolysis, polyimide film was transformed into conductive material. As the pyrolysis temperature increases, the resistivity decreases. The resistivity amounted to 9.87×10^{-3} Ωcm at

900 °C pyrolysis temperature. The resistivity of pyrolyzed polyimide in this experiment has the resistivity in the semiconducting region. From this result, pyrolyzed polyimide will be applicable to some conducting layer as a semiconducting material.

4. Mechanical Properties

In this paper, Young's modulus and the initial tensile stress of pyrolyzed polyimide were evaluated by the load-deflection test. Fig. 5 shows the schematic view of the load-deflection measurement system. Fig. 6 shows the fabrication process of pyrolyzed polyimide diaphragm. In this fabrication, 525 µm thick silicon substrate with double side silicon nitride were used as a substrate. The thickness of Silicon nitride was 2000Å. At first, the backside of silicon nitride was patterned by RIE process with CF4 gas for 75 seconds. After patterning of the silicon nitride, polyimide was spun at 2000 rpm and baked. After baking, the measured thickness of polyimide was 3.8 µm. Cr / Au were evaporated and patterned for a reflector pattern at the center of membrane for the center deflection measurement. The reflector pattern was 200 µm × 200 µm. After fabrication of the reflector, silicon anisotropically etched

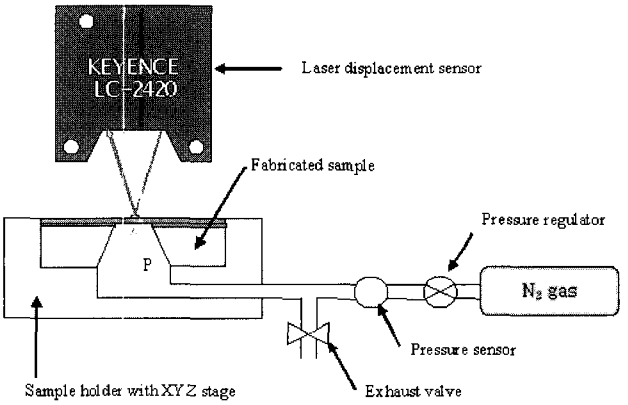
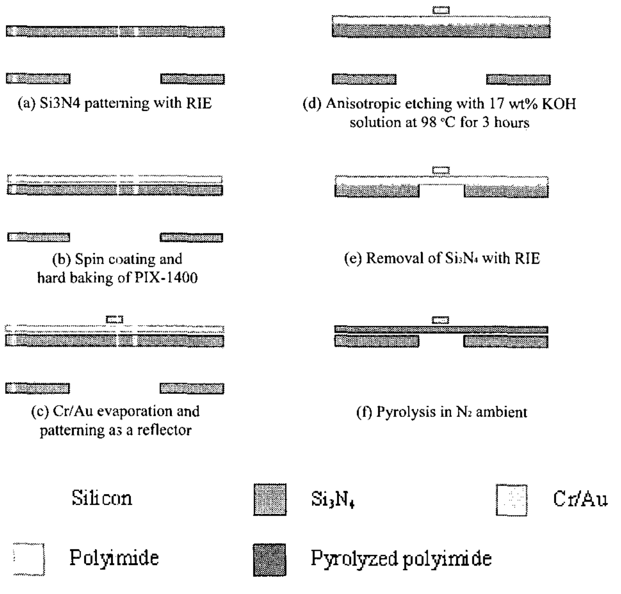


Fig. 5. Schematic view of the load-deflection measurement system for mechanical property evaluation


(a) Si3N4 patterning with RIE

(b) Spin coating and hard baking of PIX-1400

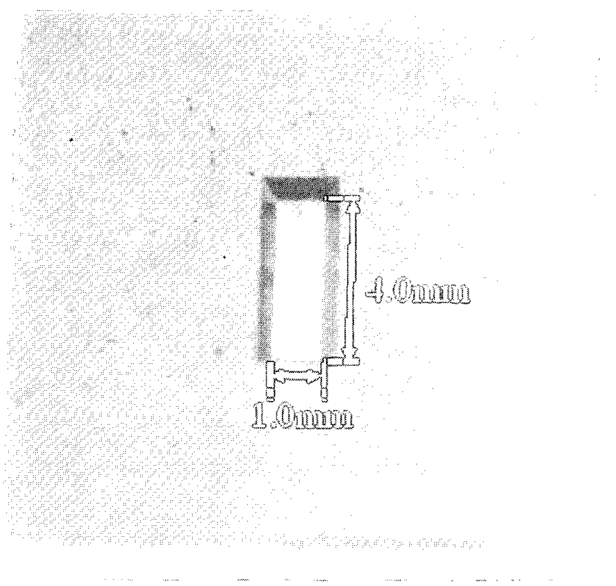
(c) Cr/Au evaporation and patterning as a reflector

(d) Anisotropic etching with 17 wt% KOH solution at 98 °C for 3 hours

(e) Removal of Si_3N_4 with RIE

(f) Pyrolysis in N_2 ambient

Fig. 6. Fabrication process of pyrolyzed polyimide diaphragm structure



(a) before pyrolysis process

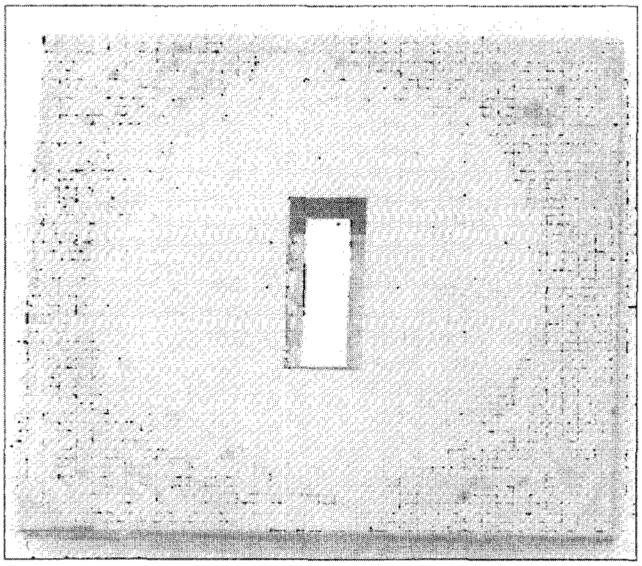

(b) after pyrolysis process

Fig. 7. Photographs of the fabricated polyimide diaphragm structure for load-deflection test

with 17 wt% of KOH etchant at 98 °C for 3 hours. Silicon nitride as a etch stopper layer under the polyimide was removed by RIE process with CF4 gas for 75 seconds. Finally, polyimide diaphragm structure was pyrolyzed. Fig. 7 shows the photographs of fabricated polyimide diaphragm structure before and after pyrolysis process. The diaphragm size is 1.0 mm × 4.0 mm. The color of pyrolyzed membrane becomes dark while an underlying meshed pattern can be seen through the transparent polyimide membrane in Fig. 7 (a). The polyimide diaphragm processed at 800 °C is shown in Fig. 7 (b).

The center deflection of the pyrolyzed polyimide membrane was measured with laser displacement sensor. Young's modulus and initial tensile stress are estimated from the comparison between the measured data and the calculated one [9]. Fig. 8 and 9 show estimated Young's modulus and initial tensile stress. The Young's modulus amounted to 67 GPa at 800 °C pyrolysis temperature if Poisson's ratio was set to be 0.3.

Above 700 °C Young's modulus gradually increases, but initial tensile stress dramatically decreases. This phenomena is highly related with annealing effect and rearrangement process among polymer chains during the pyrolysis process at high temperature for long time. As the pyrolysis temperature increases, pyrolyzed polyimide becomes more rigid and dense. But, the rearrangement process of polyimide thin film seems to be almost finished, and then annealing process seems to be progressed around 800 °C. Therefore, the initial tensile stress of thin film might be reduced.

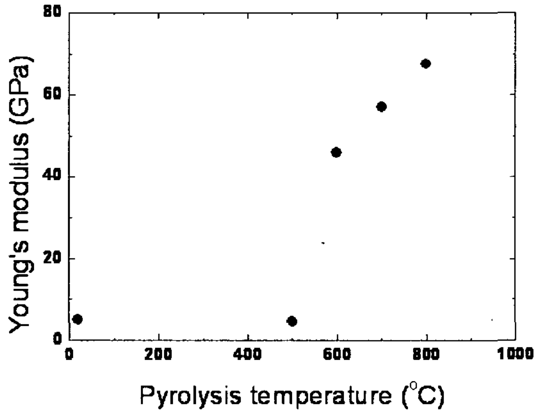


Fig. 8. Estimated Young's modulus of pyrolyzed polyimide

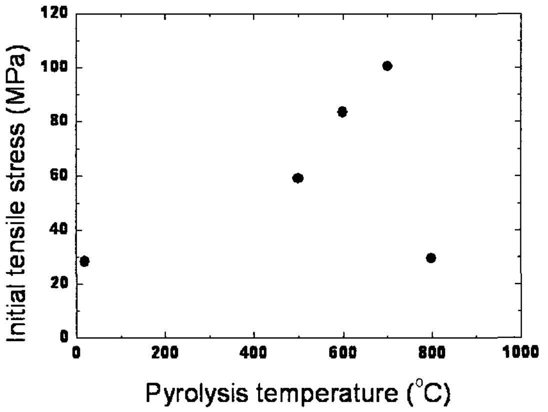


Fig. 9. Estimated initial tensile stress of pyrolyzed polyimide

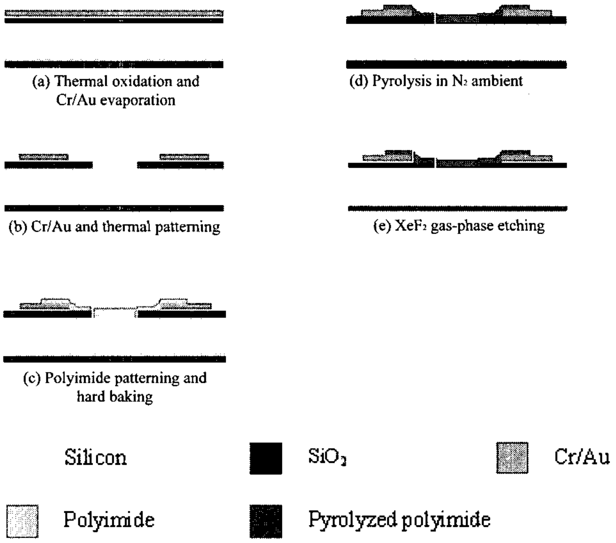


Fig. 10. Fabrication process of pyrolyzed polyimide microbridge structure

5. Microbridge as a MEMS Structure

Various attractive MEMS devices using pyrolyzed polymers will be realized if MEMS structure using pyrolyzed polymer is achieved. The microbridge structure is common structure in MEMS because the microbridge is used as a resonator, a micro heater and sensors.

In this paper, pyrolyzed polyimide microbridge structure are designed and fabricated for MEMS applications. Fig. 10 shows the fabrication process of pyrolyzed polyimide microbridge. The proposed fabrication process consists of the pyrolysis process and the sacrificial layer etching process. After sequential thermal oxidation process and Cr / Au evaporation process, metal layers and the oxide layer are patterned. Next, polyimide is patterned and pyrolyzed at 800 °C. Finally, pyrolyzed polyimide microbridge is released by XeF_2 gas-phase etching process. Fig. 11 shows a fabricated

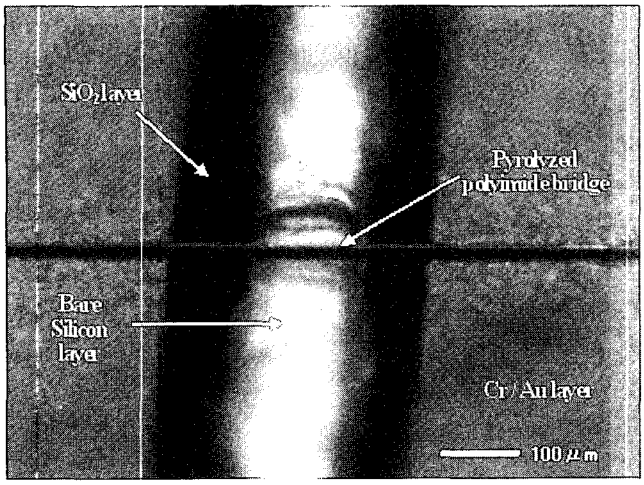


Fig. 11. Photograph of the fabricated pyrolyzed polyimide microbridge structure

microbridge structure. The length and width of the fabricated microbridge are 150 μm and 50 μm, respectively. The fabricated microbridge will be applicable to a micro heater and a resonator.

III. SUMMARY

This paper presents pyrolyzed polyimide for MEMS application among several candidates of pyrolyzed polymers. First of all, the chemical stability of pyrolyzed polyimide was investigated using major etchants and acids in MEMS fabrication process. From the measurement results of electrical and mechanical properties of pyrolyzed polyimide films, the resistivity and Young's modulus of pyrolyzed polyimide processed at 800 °C pyrolysis temperature amounted to 2.17×10^{-2} Ωcm and 67 GPa, respectively. Based on these results, it will be expected to apply pyrolyzed polyimide to MEMS because of its attractive properties such as chemical, electrical, and mechanical properties.

ACKNOWLEDGMENTS

All authors would like to thank Prof. Yu-Chong Tai and his members at California Institute of Technology for their helpful discussions.

REFERENCES

[1] H. Teoh, P. D. Metz, and W. G. Wilhelm, *Molecular Crystals and Liquid Crystals*, Vol. 83, pp. 297-306, 1982.

[2] H. B. Brom, Y. Tomkiewicz, A. Aviram, A. Broers and B. Sunners, *Solid State Communications*, Vol. 35, pp. 135-139, 1979.

[3] R. Kostecki, B. Schnyder, D. Alliata, X. Song, K. Kinoshita and R. Kötz, *Thin Solid Films*, Vol. 396, pp. 36-43, 2001.

[4] C. Z. Hu and J. D. Andrade, *Journal of Applied Polymer Science*, Vol. 30, pp. 4409-4415, 1985.

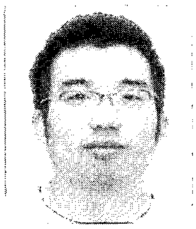
[5] S. Ranganathan, R. McCreery, S. M. Majji, and M. Madou, *Journal of Electrochemical Society*, Vol. 147, pp. 277-282, 2000.

[6] S. Konishi, M. Liger, T. A. Harder, and Y. C. Tai, *in DigestTech Papers MEMS'04 Conference*, pp. 161-164, 2004.

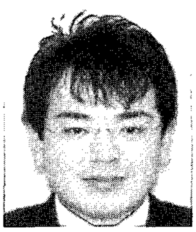
[7] M. H. Li, J. J. Wu, and Y. B. Gianchandani, *Journal of Microelectromechanical Systems*, Vol. 10, pp. 3-9, 2001.

[8] A. H. Z. Ahmed and R. N. Tait, *Journal of Vacuum Science & Technology A*, Vol. 22, pp. 842-846, 2004.

[9] O. Tabata, K. kawashima, S. Sugiyama, and I. Igarashi, *Sensors and Actuators*, vol. 20, pp. 135-141, 1989.



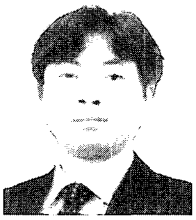
Keisuke Naka He received the BS and MS degrees in Mechanical Engineering from Ritsumeikan University, Shiga, Japan, in 2003 and 2005, respectively. He is studying as Ph.D. Candidate with Ritsumeikan University. His current research interests is pyrolyzed polymer and its application in MEMS.



Hideki Nagae He received the BS and MS degrees in Mechanical Engineering from Ritsumeikan University, Shiga, Japan, in 2003 and 2005, respectively.

Masao Ichiyanagi He received the BS degrees in Mechanical Engineering from Ritsumeikan University, Shiga, Japan, in 2004. He is studying pyrolyzed polymer and its application as a graduate, Ritsumeikan University.

Ok Chan Jeong He received his Ph. D. degree in 2004 in Control and Instrumentation Engineering from AJOU University, Suwon, Korea. He is currently a post-doctoral researcher in KONISHI MEMS Research Group, Ritsumeikan University, Japan. His current research interests include the pneumatic actuation mechanism and its application to micro actuator, micro pump and micro robot for bio medical field.



Satoshi Konishi He received the BS degree in 1991 in electronics engineering, the MS degree in 1993 and the PhD degree in 1996 in electrical engineering, from the University of Tokyo, Tokyo, Japan. He is currently Associate professor in Ritsumeikan University, Shiga, Japan, where he joined the faculty in 1996. His study is devoted to microelectromechanical systems (MEMS), especially distributed MEMS. His current research focuses on microactuator for advanced positioner, acoustic MEMS, and biomedical MEMS.