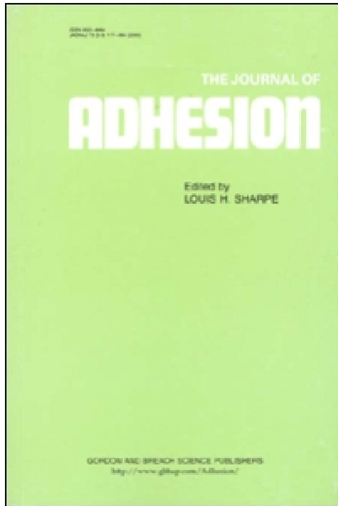
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Excimer Laser Induced Removal of Particles from Hydrophilic Silicon Surfaces

X. Wu[a]; E. Sacher[a]; M. Meunier[a]
[a] Groupe de Recherche en Physique et Technologie des Couches Minces, Département de Génie Physique, École Polytechnique de Montréal, Québec, Canada

To cite this Article Wu, X. , Sacher, E. and Meunier, M.(1999) 'Excimer Laser Induced Removal of Particles from Hydrophilic Silicon Surfaces', The Journal of Adhesion, 70: 1, 167 — 178
To link to this Article: DOI: 10.1080/00218469908010493
URL: http://dx.doi.org/10.1080/00218469908010493

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1999, Vol. 70, pp. 167–178
Reprints available directly from the publisher
Photocopying permitted by license only

© 1999 OPA (Overseas Publishers Association) N.V.
Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Downloaded At: 10:33 22 January 2011

Excimer Laser Induced Removal of Particles from Hydrophilic Silicon Surfaces*

X. WU, E. SACHER[†] and M. MEUNIER

Groupe de Recherche en Physique et Technologie des Couches Minces, Département de Génie Physique, École Polytechnique de Montréal, C.P. 6079, Succursale Centre-Ville, Montréal, Québec H3C 3A7, Canada

(Received 14 September 1998; In final form 21 December 1998)

A pulsed KrF excimer laser was used to remove several types of submicron-sized particles from silicon surfaces. Polystyrene latex particles, 0.1 μm and larger, were removed from silicon surfaces by dry laser cleaning (no water layer condensed on the surface) but SiO_2 particles could not be so removed. However, during steam laser cleaning, in which a thin film of water is deposited on the surface as both an energy transfer medium and an adhesion force reduction agent, these 0.1 – 0.2 μm SiO_2 particles were almost entirely removed. Calculations of the various forces contributing to adhesion indicate that hydrogen bonds are the major contributor to the adhesion of inorganic particles to substrate surfaces. Photoacoustic detection, using piezoelectric transducers, monitored the surface vibrations induced by the laser pulses.

Keywords: Excimer laser; steam and dry cleaning; submicron particulate removal; photoacoustic detection; hydrogen bonding

INTRODUCTION

As the requirements for increased device performance and reliability have become more and more stringent in the era of VLSI and ULSI

---

*Presented at the 21st Annual Meeting of The Adhesion Society, Inc., Savannah, Georgia, USA, February 22–25, 1998.

[†]Corresponding author. Tel.: 514-340-4711, Ext. 4858, Fax: 514-340-3218, e-mail: sacher@phys.polymtl.ca

silicon circuit technology, there is a continuing need to develop more effective techniques to clean smaller and smaller particulates from microelectronic surfaces [1]. More than 50% of yield losses in integrated circuit fabrication are due to micro-contamination [2]. Such particles can cause surface conduction, decrease minority carrier lifetimes during high-temperature processing, or can cause blocking and masking during photolithography [1]. Traditional cleaning techniques may damage delicate parts because they rely on mechanical contact forces and chemical reaction, and they do not efficiently remove submicron particles [3–5].

Laser cleaning techniques demonstrate a high potential for this task because of their high efficiency, simplicity, speed and low cost [6, 7]. There are two types of laser cleaning methods used to date [6–10]. The first, called steam laser cleaning, has a high cleaning efficiency, made possible by the use of a thin film of water as an energy transfer medium and adhesion force reduction agent. The second is dry laser cleaning which is simpler, in that no liquid is involved; it is compatible with cluster tools. In order to help understand the laser cleaning mechanism, several techniques have been developed to measure the photoacoustic waves induced by laser pulses incident on the substrate surface [11–13]. The piezoelectric transducer is one of them. It is simple and can monitor surface vibrations during laser cleaning.

In preliminary studies, we reported that several kinds of submicron-sized particles could be removed during steam cleaning by a CO_2 laser [14, 15]. At the CO_2 laser wavelength (10.6 μm), the laser energy is strongly absorbed by the water film and partially absorbed by the silicon wafer. To compare with a process in which the laser energy is absorbed at the substrate surface, we have used a KrF excimer laser because, at the wavelength used (248 nm), water is transparent and the silicon substrate has a very short optical penetration length (5.5 nm). Other advantages of the excimer laser are that it has a uniform laser beam and high photon energy (5 eV). In the work we report here, 0.1 μm polystyrene latex (PSL) particles were efficiently removed from a silicon surface by dry laser cleaning while 0.1 – 0.2 μm SiO_2 particles could only be efficiently removed by steam laser cleaning. We have determined the photoacoustic wave spectra for the two cleaning methods and use it to understand the two laser cleaning techniques.

Downloaded At: 10:33 22 January 2011

EXPERIMENT

The experimental setup is shown schematically in Figure 1. Optical pulses from an MPB Technologies, Inc., AQX-150 excimer laser, operating at the KrF wavelength of 248 nm, with a 22 ns pulse width at half maximum (FWHM) and 200 mJ of pulse energy, were directed onto a 6 mm × 18 mm aperture which was imaged onto the sample wafer using a 100 mm focal length lens. The energy fluence of the laser pulse was monitored by using a beam splitter and a joulemeter in front of mirror 1. The wafer sample was mounted face down on a computer-controlled XYZ stage so that the area irradiated by the laser could be varied by scanning in the XY directions, and laser energy densities on the wafer surface could be varied, in the range 50–1000 mJ/cm^2, by changes in the Z-axis position.

A specially-designed liquid film deposition system was used to coat the sample at the irradiation location prior to laser exposure. This system utilized a burst of nitrogen gas into a stainless steel chamber half-filled with deionized (DI) water typically kept at 40°C by a stainless steel isolated heater; the water temperature was measured by a stainless steel isolated thermometer. The nitrogen gas input of

Downloaded At: 10:33 22 January 2011

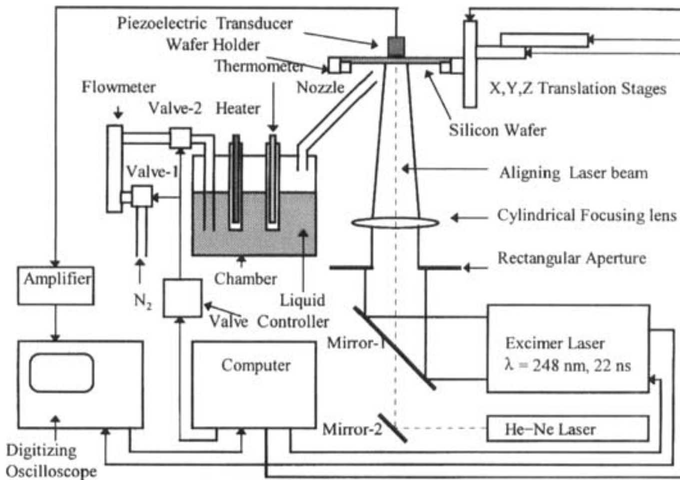


FIGURE 1 Experimental setup for excimer laser cleaning and the measurement of photoacoustic waves.

4700 ml/min entrained a controlled volume of water vapor, which was directed toward the wafer surface by a stainless steel nozzle, kept at 45°C. Gas valves controlled by computer were opened for 0.2 seconds, and water vapor condensed as a thin liquid film, several microns thick, on the colder wafer surface. Three laser pulses, separated by 0.1 seconds, were triggered 0.1 seconds after the deposition of the water vapor. During laser cleaning, the wafer was linearly stepped after each water vapor burst. The overlap of the laser beam was kept at $\sim 10\%$. We used multiple scanning in order to cover the gaps between previous step scanning and to remove any recontaminating particles. The laser energy flux was carefully maintained below the silicon surface damage threshold that we determined, about 360 mJ/cm^2 for dry cleaning and 200 mJ/cm^2 for steam cleaning.

The samples were 100 mm ⟨100⟩ silicon wafers, whose surfaces were cleaned and made hydrophilic using a modified RCA recipe [15]. The particles used to contaminate the surface artificially were Particle Measuring System, Inc., 0.1 µm polystyrene latex (PSL) and Beta Diamond Corp., 0.1 – 0.2 µm agglomerated SiO_2. The particles were deposited onto the wafer surface using a Particle Measuring System, Inc., particle generator. A Particle Measuring System, Inc., SAS 3600 laser scanning surface inspection system was used to count the particles on the wafer surface.

In the photoacoustic wave (PAW) experiments, a Panametrics, Inc., V1091 broadband piezoelectric transducer was attached to the wafer backside with vacuum grease used as the transducer coupling medium. The signal from the transducer was fed into a HP 54201D digitizing oscilloscope (at a sampling rate of 200 MHz and a bandwidth of 300 MHz) either directly, or through a HP 8447A preamplifier for low-intensity signals.

RESULTS

The evaluation of the removal efficiency was carried out in a 30 mm circle inside a 50 mm × 50 mm cleaned square. Particle densities, for PSL and SiO_2 on the silicon wafer surface, as a function of their size distributions, before and after dry and steam laser cleaning are found in Figure 2. Almost all the PSL particles ≥ 0.1 µm were removed by

Downloaded At: 10:33 22 January 2011

dry cleaning at 326 mJ/cm^2 but the dry cleaning of SiO_2 particles was inefficient. However, using steam cleaning with a laser energy flux reduced to 180 mJ/cm^2, most of the SiO_2 particles $\geq 0.1\,\mu m$ were removed; it was not necessary to use steam cleaning to remove PSL particles from the silicon surface because they were essentially completely removed by dry cleaning. Any particles remaining after

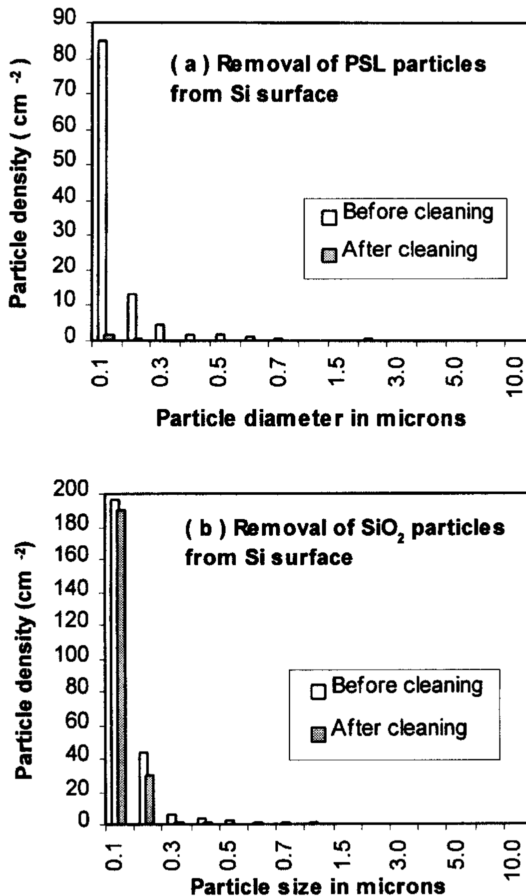


FIGURE 2 (a) PSL particle densities before and after dry laser cleaning. The laser energy flux was 326 mJ/cm^2, 2 cleaning cycles; (b) SiO_2 particle densities before and after dry laser cleaning. The laser energy flux was 314 mJ/cm^2, 4 cleaning cycles; (c) SiO_2 particle densities before and after steam laser cleaning. The laser energy flux was 180 mJ/cm^2, 5 cleaning cycles.

Downloaded At: 10:33 22 January 2011

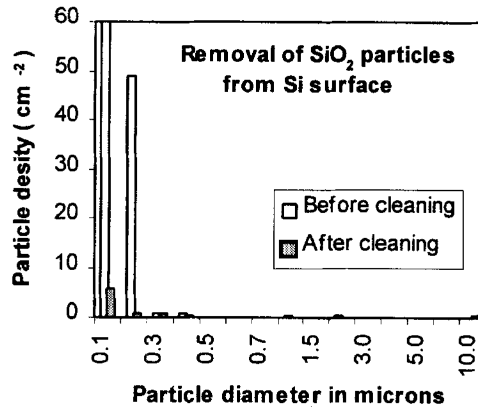


FIGURE 2 (Continued).

Downloaded At: 10:33 22 January 2011

cleaning may be due to several sources: strongly-adhering original particles, recontamination by the ejected particles near the surface, a transfer from adjacent uncleaned areas and contamination by the steam cleaning liquid deposition system. We used the particle density remaining after cleaning to quantify the cleaning efficiency.

In our photoacoustic experiments, the piezoelectric transducer was placed at different locations on the silicon wafer backside. We found that the PAW signal propagated along the substrate surface, perpendicular to the laser focus line, and was reflected at the wafer edge. These results were similar to the visual results of Al_2O_3 powder patterns in a recent paper [16] but, in our case, we used the laser scanning surface inspection system to analyze a much lower surface density of particles (PSL and SiO_2) along the PAW signal propagating path. We found that only those particles directly in the laser beam were removed, although the energy even a significant distance away was sufficient to do so.

Figure 3 shows the PAW signal for dry and steam laser cleaning detected by the piezoelectric transducer located at the center of the silicon wafer backside, directly opposite the laser beam. The peak value of the PAW signal detected during steam cleaning at a laser energy flux of 187 mJ/cm^2 was about two times greater than that detected during dry cleaning at a similar laser energy flux of 195 mJ/cm^2. It was necessary to use a laser energy flux of 310 mJ/cm^2 during dry cleaning for the PAW

signal to reach the same level as that during steam cleaning at a laser energy flux of 187 mJ/cm^2.

DISCUSSION

From our experiments, we conclude that PSL particles may be removed by dry cleaning while SiO_2 particles can only be removed by steam cleaning. We also found that the PAW signal at any laser flux

Downloaded At: 10:33 22 January 2011

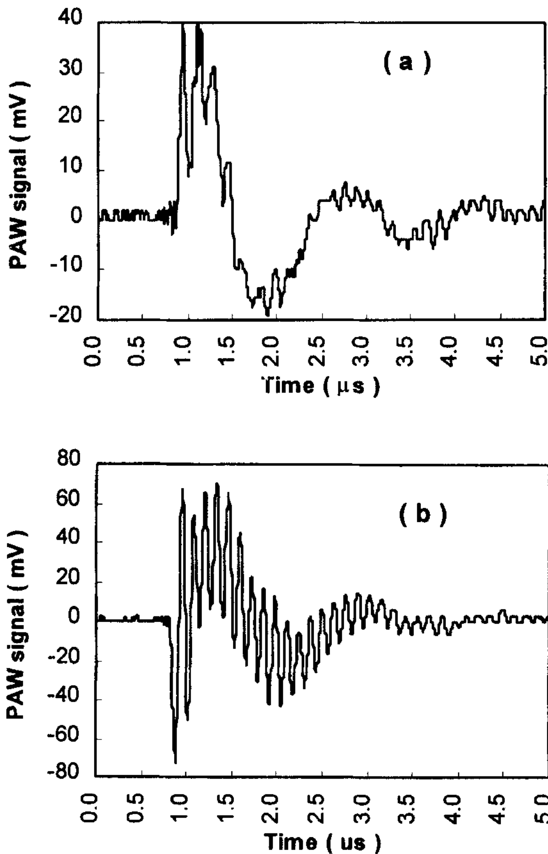


FIGURE 3 The photoacoustic wave signal: (a) dry laser cleaning at a laser energy flux of 195 mJ/cm^2; (b) steam laser cleaning at a laser energy flux of 187 mJ/cm^2; (c) dry laser cleaning at a laser energy flux of 310 mJ/cm^2.

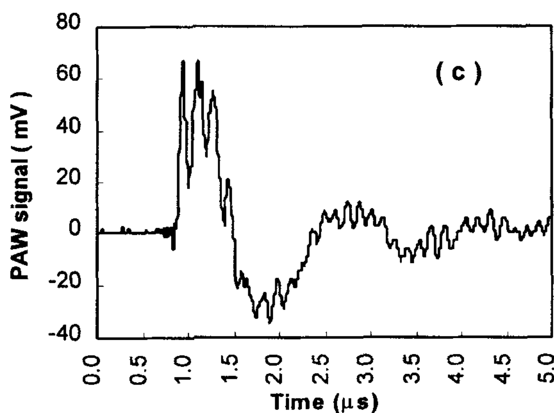


FIGURE 3 (Continued).

Downloaded At: 10:33 22 January 2011

was larger during steam clean. In this section, we will briefly explain these experimental results. Several review papers on particle adhesion to various substrate surfaces [17–19] suggest that van der Waals, capillary and electrostatic forces were involved in holding particles to the substrate surface. The van der Waals force consists of two terms: one term treats the particle as a non-deforming sphere while the other considers particle deformation; usually, the second term is dominant. The deformation area can be calculated using the JKR model [20] but this does not appear suitable for PSL particles [21]. We use the equations given in these papers, plus experimental deformation data on PSL [21, 22], to calculate the adhesion forces of 0.2 μm PSL and SiO_2 on silicon substrate surfaces; the PSL contact radius was found [22] to increase slowly with the residence time of the particle on the surface but our residence time, invariably less than 3 hours, was too short to cause a noticeable change in the contact radius. The results are given in the Table I. We find that the van der Waals force deformation term is predominant for both kinds of particles; in comparison, capillary forces are much smaller and electrostatic forces may be neglected. It should be noted that the van der Waals force of PSL is much larger than that of SiO_2 because PSL is a softer material and has a much larger deformation. Based on these calculations, the PSL particles should be more difficult to remove, but the laser cleaning experiments give the opposite results. To explain this contradiction, we

TABLE I The adhesion forces of 0.2 μm PSL and SiO_2 particles on the silicon surface

Adhesion forces	*Dry cleaning*		*Steam cleaning*
	PSL particles (0.2 *μm*)	*SiO_2 particles* (0.2 *μm*)	*SiO_2 particles* (0.2 *μm*)
van der Waals (deformation)	160 mdyn	17 mdyn	8.9 mdyn
van der Waals (non-deformation)	1.4 mdyn	2.7 mdyn	1.4 mdyn
Capillary	4.7 mdyn	9.0 mdyn	0
Electrostatic	0.004 mdyn	0.004 mdyn	0.35 mdyn
Chemical Bonds	none	surface hydroxyl	surface hydroxyl

consider the adhesion force contribution of hydrogen bonding between the hydroxyl group on the surfaces of inorganic particles and those on the silicon surface [17, 23, 24].

Many solid surfaces contain potential hydrogen bond donors and acceptors. Because hydrogen bond formation has a low activation energy, it occurs at room temperature, and the interaction of inorganic particles and substrate surfaces *via* hydrogen bonding is possible [23]. Water viscosity experiments have demonstrated the existence of hydrogen bonds between spherical and flat silica surfaces [25]. Although the hydrogen bond is not a particularly strong bond ($\sim$ 5 kcal/mole [26]), it is, nonetheless, stronger than a van der Waals bond ($\sim$ 1 kcal/mole [27]). Thus, hydrogen bonding may play an important role in the adhesion of inorganic particles to substrate surfaces. This does not occur for the PSL particles because there is no hydrogen bond donor/ acceptor group on the PSL surface. More detailed discussions will be published in a subsequent paper [28].

During the laser pulse, both particle and substrate absorb laser energy and are heated immediately. Sudden thermal expansions of both particle and substrate then take place over a very short time duration, through the thermoelastic effect [29]. It leads to the acceleration and ejection of PSL particles from the surface. For SiO_2 particles, the removal force is not strong enough to overcome the very large chemical adhesion force due to hydrogen bonding between substrate and particle, so most particles bound to the silicon surface cannot be removed by dry laser cleaning.

During steam laser cleaning, the particles are covered by a thin film of water. Due to electrical shielding [16, 18], the van der Waals force is

Downloaded At: 10:33 22 January 2011

reduced, in our case, by about a factor of two; capillary forces are nullified, and direct hydrogen bonding from particle to surface may be replaced by bonding to free water molecules. This is one reason why surface vibrations having the same amplitudes, as shown in Figures 3(b) and (c), could remove SiO_2 particles only during steam cleaning; the values of the adhesion forces for SiO_2 during steam cleaning are also given in Table I. On laser exposure, except for that fraction used in thermal expansion, the laser energy is transferred to the liquid film. This transient heating of the deposited liquid film leads to its explosive evaporation at the interface. Bubble growth and collapse generate high pressure pulses and direct particles away from the substrate surface. The increase of the PAW signal during steam cleaning, as shown in Figures 3(a) and (b), presents an additional removal force due to the creation of bubble pressure during liquid film explosive evaporation. When the PAW signal propagates along the surface, the particles held tightly to the substrate surface cannot be removed, although the particles loosely connected in multiple layers can easily be cleaned. The photon energy of the excimer laser, 5 eV, is much higher than that of the hydrogen bonds (0.1 eV) which hold the particles to the silicon surface; the laser energy is capable of breaking the hydrogen bonds. Considering that bubbles are generated only in the laser beam, the total removal forces can overcome the hydrogen bonding forces only in that area.

Downloaded At: 10:33 22 January 2011

CONCLUSIONS

We have removed 0.1 μm PSL particles from silicon surfaces by fast thermal expansion during dry laser cleaning, but 0.1 – 0.2 μm SiO_2 particles could not be so removed. We suggest there are stronger hydrogen bonding adhesion forces between SiO_2 particles and the hydrophilic silicon surface. On steam laser cleaning, the adhesion forces were greatly reduced, and the explosive evaporation of the deposited liquid film generated additional removal forces through bubble growth and collapse, permitting the removal of SiO_2 particles. Photoacoustic wave measurements demonstrate that steam laser cleaning generates higher PAW signals. The breaking of hydrogen bonds by direct laser irradiation and heating in the laser beam contribute to the local cleaning efficiency.

Acknowledgements

The authors thank J. P. Lévesque for his technical assistance and Kostas Piyakis for his aid in the design of the computer interface and in the analysis of the data. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

References

[1] Kern, W. and Tolliver, D., In: *Handbook of Semiconductor Wafer Cleaning Technology*. Kern, W., Ed. (Noyes Publications, Park Ridge, New Jersey, 1993), pp. 3, 68 and 595.
[2] Kern, W., *J. Electrochem. Soc.* **137**, 1887 (1990).
[3] Bardina, J., In: *Particles on Surfaces*, Vol. 1, Mittal, K. L., Ed. (Plenum, New York, 1988), p. 329.
[4] Ohmori, T., Fukumoto, T., Kato, T., Tada, M. and Kawaguchi, T., *J. Electrochem. Soc.* **137**, 399C (1989).
[5] Ross, P. E., *Sci. Amer.* p. 86 (June, 1990).
[6] Zapka, W., Ziemlich, W. and Tam, A. C., *Appl. Phys. Lett.* **58**, 2217 (1991).
[7] Imen, K., Lee, S. J. and Allen, S. D., *Appl. Phys. Lett.* **58**, 203 (1991).
[8] Tam, A. C., Leung, W. P., Zapka, W. and Ziemlich, W., *J. Appl. Phys.* **71**, 3515 (1992).
[9] Kelley, J. D., Stuff, M. I., Hovis, F. E. and Linford, G. J., *SPIE Proc.* **1415**, 211 (1991).
[10] Park, H. K., Grigoropoulos, C. P., Leung, W. P. and Tam, A. C., *IEEE Trans. Com. Pack. Manuf. Technol.* **A17**, 631 (1994).
[11] Leung, W. P. and Tam, A. C., *Appl. Phys. Lett.* **60**, 6 (1992).
[12] Tam, A. C., Do, N., Klees, L., Leung, P. T. and Leung, W. P., *Opt. Lett.* **17**, 1809 (1992).
[13] Yavas, O., Leiferer, P., Park, H. K., Grigoropoulos, C. P., Poon, C. C., Leung, W. P., Do, N. and Tam, A. C., *Appl. Phys.* **A58**, 407 (1994).
[14] Heroux, J. B., Boughaba, S., Ressejac, I., Sacher, E. and Meunier, M., *J. Appl. Phys.* **79**, 2857 (1996).
[15] Boughaba, S., Wu, X., Sacher, E. and Meunier, M., *J. Adhesion* **61**, 293 (1997).
[16] Kolomenskii, A. K. and Maznev, A. A., *J. Appl. Phys.* **77**, 6052 (1995).
[17] Krupp, H., *Advan. Colloid Interface Sci.* **1**, 111 (1967).
[18] Bowling, R. A., *J. Electrochem. Soc.* **132**, 2209 (1985).
[19] Ranade, M. B., *Aerosol Sci. Tech.* **7**, 161 (1987).
[20] Johnson, K. L., Kendall, K. and Roberts, A. D., *Proc. R. Soc. London* **A324**, 301 (1971).
[21] Rimai, D. S. and DeMejo, L. P., *Ann. Rev. Mater. Sci.* **26**, 21 (1996).
[22] Krishnan, S., Busnaina, A. A., Rimai, D. S. and Demejo, L. P., *J. Adhesion Sci. Technol.* **8**, 1357 (1994).
[23] Knozinger, H., In: *The Hydrogen Bond*, Schuster, P., Zandel, G. and Sandorfy, C., Eds. (North-Holland, New York, 1976), part I.
[24] Sugino, R., Okui, Y., Okuno, M., Shigeno, M., Sato, Y., Ohsawa, A. and Ito, T., *IEICE Trans. Electron.* **E75-C**, 829 (1992).
[25] Peschel, G. and Aldfinger, K. H., *J. Colloid Interface Sci.* **34**, 505 (1970).
[26] Pauling, L., *The Nature of the Chemical Bond and the Structure of Molecules and Crystal* (Cornell Univ. Press, New York, 1960), Chap. 12.

Downloaded At: 10:33 22 January 2011

[27] Israelachvili, J., *Intermolecular and Surface Forces* (Academic, New York, 1991), Chap. 8.
[28] Wu, X., Sacher, E. and Meunier, M., to *J. Appl. Phys.* submitted.
[29] Burgreen, D., *Elements of Thermal Stress Analysis* (C. P. Press, Jamaica, New York, 1971), pp. 1-28, 89-91.

Downloaded At: 10:33 22 January 2011