Vacuum Ultraviolet Irradiation Treatment for Reducing Gold–Gold Bonding Temperature

Akiko Okada^{1,*1}, Shuichi Shoji¹, Masatsugu Nimura^{1,*1}, Akitsu Shigetou², Katsuyuki Sakuma³ and Jun Mizuno^{1,*2}

¹Department of Nanoscience and Nanoengineering, Waseda University, Tokyo 169-8555, Japan

²National Institute for Materials Science, Tsukuba 305-0044, Japan

³Microelectronics Division, IBM Corporation, NY 12533, USA

Low-temperature Au–Au bonding was achieved under vacuum ultraviolet irradiation in the presence of oxygen gas (VUV/O₃). The Au surfaces obtained after the VUV/O₃ treatment were analyzed by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) measurements. The results indicate that the amount of carbon-based contaminants was dramatically decreased and that there was no serious damage to Au surfaces caused by the VUV/O₃ treatment. The Au–Au bonding temperature was successfully reduced to 150°C after the VUV/O₃ treatment. The average shear strength was approximately 56 MPa, and cross-sectional scanning electron microscopy (SEM) images of the bonded samples confirmed the absence of voids and cracks. Therefore, VUV/O₃ treatment is highly effective for achieving low-temperature Au–Au bonding. [doi:10.2320/matertrans.MF201313]

(Received February 4, 2013; Accepted August 20, 2013; Published October 4, 2013)

Keywords: bonding, gold, flip chip, micro-bump, three-dimensional integration, vacuum ultraviolet

1. Introduction

Three-dimensional (3D) chip-stacking technology is an attractive means of reducing interconnect delays in future integrated circuits (ICs) because through-silicon vias (TSVs) and micro-bumps offer shorter wiring distances between the stacked chips.^{1–7)}

Low-temperature bonding is important for 3D chip stacking in order to avoid various problems arising at high temperatures such as thermal damage to the circuit elements, chip warping and thermal expansion, which may lower the alignment accuracy. Conventionally, proposed low-temperature Au–Au bonding techniques have included plasma irradiation⁸⁾ or ultrasonic bonding.⁹⁾ However, plasma irradiation cleaning requires high-vacuum conditions (pressure less than 10 Pa),¹⁰⁾ which reduces the throughput of the bonding process. On the other hand, it is difficult to bond large chips with many bumps using ultrasonic bonding because the ultrasonic vibration is dispersed on each bump, decreasing the intensity of the vibrations. Furthermore, it is difficult to align chips with a high degree of accuracy because of the ultrasonic vibration.

Vacuum ultraviolet irradiation treatment in the presence of oxygen gas (VUV/O₃) can prevent such problems.¹¹⁾ The concept of this treatment is to remove carbon-based organic contaminants with the oxygen radicals excited by VUV, thus causing oxidative degradation and volatilization of the contaminants. This treatment causes no serious damage to the cleaned parts and can be used for wafer-level cleaning. In addition, the treatment system needs only low-vacuum conditions (pressure of 30 kPa), so the throughput of the bonding process can be higher than that obtained through plasma irradiation cleaning. In this paper, VUV/O₃ treatment was studied as a technique for reducing the Au–Au bonding temperature.

Fig. 1 Schematic illustration of an upper Si chip with Au bumps and a lower Si chip with evaporated Au.

2. Materials and Procedures

2.1 Materials

Figure 1 shows a cross-sectional schematic illustration of an upper silicon chip with Au bumps and a lower Si substrate with evaporated Au. The diameter, pitch and height of the Au bumps are 10, 100 and 1.7 μm, respectively. The bump count on the chip is 900. Furthermore, 30-nm-thick Ti and 300-nm-thick Au films were evaporated on the lower silicon substrate.

The process for fabrication of an Au bump is shown schematically in Fig. 2 and proceeds as follows: (a) a seed layer composed of 30-nm-thick Ti and 100-nm-thick Au layers is evaporated on a Si chip. (b) A photoresist (AZP4620, AZ Electronic Materials Co., Ltd.) is patterned using photolithography. (c) Au is electroplated within the resist pattern. (d) The resist is removed by an organic solvent. (e) The seed layer is removed by performing Ar ion milling.

Figure 3 shows an optical micrograph of a chip with Au bumps and an SEM image of a single Au bump.

2.2 Procedures

2.2.1 VUV/O₃ surface treatment

Figure 4 shows a cross-sectional illustration of the VUV/O₃ treatment system (Ushio UER 20-172), which is composed of a lamp house and an irradiation chamber. The UV light has a central wavelength of 172 nm and a full width at half maximum (FWHM) of 14 nm. Light with a wave-

*1Graduate Student, Waseda University

*2Corresponding author, E-mail: mizuno@waseda.jp

Fig. 2 Schematic diagram of process for fabrication of Au bumps.

Fig. 3 (a) Optical micrograph of chip with Au bumps and (b) SEM image of a single Au bump.

length shorter than 175 nm can produce oxygen radicals by directly decomposing oxygen. The UV light, transmitted through the glass window of the lamp house, causes chemical reactions in the irradiation chamber. Oxygen radicals generated by oxygen and ozone cause oxidative degradation that volatilizes the contaminants. Thus, organic contaminants were removed via these reactions. Before flip-chip bonding, both the upper chip and the lower substrate were subjected to VUV/O₃ treatment. The VUV/O₃ treatment conditions are shown in Table 1. The treatment was carried out at room temperature in a chamber with an ozone pressure of 30 kPa. The exposure time for each sample was 5 min.

2.2.2 Bonding process

The Au–Au bonding was carried out both with and without VUV/O₃ treatment such that the effect of the VUV/O₃ treatment could be evaluated. After both an upper chip and

Fig. 4 Cross-sectional illustration of VUV/O₃ treatment system.

Table 1 VUV/O₃ treatment conditions.

Lamp power P/W	20
UV wavelength λ/nm	172
Light intensity $E/\text{mW}\cdot\text{cm}^{-2}$	10
Exposure time t/min	5
Temperature $T/^\circ\text{C}$	24
Chamber pressure under oxygen gas p/Pa	3.0×10^4

Fig. 5 Cross-sectional illustration of bonding equipment.

Table 2 Bonding conditions.

Temperature $T/^\circ\text{C}$	150
Bonding pressure P/MPa	262
Bonding time t/min	10, 20
Chamber pressure P_c/Pa	<100

a lower chip were subjected to the VUV/O₃ treatment, the chip with Au bumps was bonded to the evaporated-Au chip surface as soon as possible to prevent adhesion of contaminants from the ambient air after the VUV/O₃ treatment. Figure 5 shows a cross-sectional illustration of the bonding equipment. First, the processing chamber was evacuated to a pressure of less than 100 Pa. Then, the bonding pressure and temperature were applied. Both the upper chip and the lower chip were heated by carefully controlled electric heaters above and below the chips. The bonding conditions are shown in Table 2. The bonding temperature was 150°C, and the bonding times, which are the times for which the samples were kept at the bonding temperature, were 10 and 20 min. The bonding pressure was 262 MPa.

Fig. 6 (a) Cross-sectional illustration and (b) photograph of the die shear test setup.

Fig. 7 AFM image of untreated (a) evaporated-Au chip surface and (b) Au bump surface.

Fig. 8 AFM image of VUV/O₃-treated (a) evaporated-Au chip surface and (b) an Au bump surface.

2.2.3 Characterization

Atomic force microscopy (AFM) measurements (using a SHIMADZU SPM-9600) were performed to examine the surface roughness and morphology of the Au bumps and the evaporated-Au chip surface before and after VUV/O₃ treatment.

X-ray photoelectron spectroscopy (XPS) was used to investigate the composition of the Au surfaces before and after VUV/O₃ treatment. XPS measurements (using a Japan Electron Optics Laboratory JPS-9010TR) were performed using Mg K α (1253.6 eV) radiation at 100 W (10 kV, 10 mA).

After the bonding, the shear strengths of the samples, bonded both with and without VUV/O₃ treatment, were measured by performing shear strength tests (using a Dage Japan Dage-4000). Figure 6 shows a cross-sectional illustration and a photograph of the die shear test setup. The bonded sample was horizontally strained by the shear tool, and the stress at rupture was measured. The shear tool speed in the die shear test was 50 $\mu\text{m/s}$.

3. Results and Discussion

3.1 Surface analysis

Figures 7 and 8 show AFM images of the evaporated-Au chip surface and an Au bump surface, respectively, before and after VUV/O₃ treatment. The AFM-scanned area was $5 \times 5 \mu\text{m}$. The root mean square (RMS) surface roughness of the untreated evaporated-Au chip surface and an untreated Au bump were 1.58 and 35.5 nm, respectively. The RMS surface roughness of the VUV/O₃-treated evaporated-Au chip surface and a VUV/O₃-treated Au bump were 2.07 and 36.3 nm, respectively. The differences between the surface roughness values before and after VUV/O₃ treatment were minimal.

Fig. 9 Narrow-scan (a) C 1s and (b) Au 4f XPS spectra for the evaporated-Au chip surface before and after VUV/O₃ treatment.

Figures 9 and 10 show narrow-scan C 1s and Au 4f XPS spectra before and after VUV/O₃ treatment of the evaporated-Au chip surface and an Au bump surface, respectively. In Figs. 9(a) and 10(a), there is a large peak

Fig. 10 Narrow-scan (a) C 1s and (b) Au 4f XPS spectra for the Au bump surface before and after VUV/O₃ treatment.

attributable to C–C bonds at 284.6 eV and relatively small peaks attributable to C–O bonds at 286.5 eV and O–C=O bonds at 288.7 eV. After VUV/O₃ treatment, the C–C and C–O bond peak strengths dramatically decreased, which shows that organic contaminants on the evaporated-Au chip surface and on the Au bump surface were removed by the VUV/O₃ treatment. The reason that permits removal of organic contaminants by the treatment is considered to be the following. The bond energies of C–C bonds and C–O bonds are 348 and 358 kJ/mol, respectively. Therefore, the 172 nm VUV light, whose photon energy is 697.5 kJ/mol, has sufficient energy to rupture the chemical bonds of molecules, thereby forming organic contaminants. Thus, organic contaminants were split into smaller components by the VUV light. After this photodissociation reaction, oxygen radicals, which were also produced by photodissociation of oxygen and ozone molecules, reacted with those organic components and formed water and carbon oxides. These compounds were volatilized and eventually removed at the surface. Figures 9(b) and 10(b) show two distinct peaks corresponding to Au 4f_{7/2} at 84.0 eV and Au 4f_{5/2} at 87.9 eV. The peak intensity in the Au 4f spectra increased after the VUV/O₃ treatment, which means that the purity of the Au on the surfaces increased because organic contaminants were removed. As shown in Tables 3 and 4, the carbon concentration decreased by almost 30% and the Au concentration increased by almost 23% after the VUV/O₃ treatment.

Table 3 Surface elemental compositions of evaporated-Au chip surface determined by XPS analysis.

Surface treatment	Atomic concentration %		
	C	O	Au
No treatment	51.6	8.5	39.9
VUV/O ₃ treatment	18.0	17.6	64.4

Table 4 Surface elemental compositions of Au bump surface determined by XPS analysis.

Surface treatment	Atomic concentration %		
	C	O	Au
No treatment	44.0	9.0	47.1
VUV/O ₃ treatment	18.1	12.3	70.0

Table 5 Shear strengths of samples bonded with and without VUV/O₃ treatment.

Surface treatment	Bonding time <i>t</i> /min	Shear strength <i>P</i> /MPa
No treatment	10	—
	20	—
VUV/O ₃ treatment	10	55.94
	20	57.85

3.2 Shear strength testing

The shear strengths per unit area of the samples bonded with and without VUV/O₃ treatment are shown in Table 5. The Au bumps were bonded to the evaporated-Au chip surface at 150°C after the VUV/O₃ treatment. The upper chips were easily broken away from the lower substrates using tweezers when no VUV/O₃ treatment was performed. This is because organic contaminants remained at the interface during the application of bonding pressure, and prevented Au atoms from diffusing through the contaminant layer to the other side when no treatment was performed. In contrast, the Au bump surface got closer to the evaporated-Au chip surface during the bonding process due to the removal of carbon-based contaminants by the VUV/O₃ treatment. The treatment promoted interface diffusion, thus forming stronger metallurgical bonds between the surfaces over a wider bonding area.

Figures 11 and 12 show cross-sectional SEM images of the samples bonded for 10 and 20 min, respectively, after VUV/O₃ treatments. As shown in the figures, nanometer-sized voids are present at the Au–Au bonding interface. However, there are no obvious voids in a large section of the bonding area. This is because the RMS surface roughness of the Au bump is about 36 nm, which is more than ten times larger than that of the Au thin film. Therefore, the surface asperities of the Au bumps could not deform completely. Furthermore, there were no specific differences between the shear strengths and the bonding interfaces of the samples bonded for 10 and 20 min. These results demonstrate that sufficient interfacial diffusion was promoted within 10 min.

Fig. 11 Cross-sectional SEM images of (a) a sample bonded for 10 min and (b) the bonding interface of the sample.

Fig. 12 Cross-sectional SEM images of (a) a sample bonded for 20 min and (b) the bonding interface of the sample.

4. Conclusion

In this study, Au–Au bonding was achieved at 150°C by performing VUV/O₃ treatments. XPS and AFM results showed that the amounts of carbon-based organic contaminants were significantly decreased by the VUV/O₃ treatment without any damage to the Au surfaces. Furthermore, the SEM observation showed no obvious voids at the bonding interface. These results indicate that interface diffusion was promoted by the removal of organic contaminants during the VUV/O₃ treatment, which led to the formation of strong metallurgical bonds at the bonding interface. Therefore, VUV/O₃ treatment is highly effective for reducing the Au–Au bonding temperature.

Acknowledgments

This work is partly supported by Japan Ministry of Education, Culture, Sports, Science and Technology (MEXT) Grant-in-Aid for Scientific Basic Research (S) No. 23226010 and Specially Promoted Research “Establishment of Electrochemical Device Engineering”. The authors would also like to acknowledge support and encouragement for members of the Nano Technology Research center.

REFERENCES

- 1) K. Sakuma, N. Nagai, M. Saito, J. Mizuno and S. Shoji: *IEEJ Trans. Electr. Electron. Eng.* **4** (2009) 339–344.
- 2) M. Koyanagi, H. Kurino, K. W. Lee, K. Sakuma, N. Miyakawa and H. Itani: *IEEE Micro* **18** (1998) 17–22.
- 3) R. R. Tummala: *IEEE Trans. Adv. Packag.* **27** (2004) 241–249.
- 4) K. Sakuma, P. S. Andry, C. K. Tsang, S. L. Wright, B. Dang, C. S. Patel, B. C. Webb, J. Maria, E. J. Sprogis, S. K. Kang, R. J. Polastre, R. R. Horton and J. U. Knickerbocker: *IBM J. Res. Dev.* **52** (2008) 611–622.
- 5) G. H. Loh, Y. Xie and B. Black: *IEEE Micro* **27** (2007) 31–48.
- 6) J. U. Knickerbocker, P. S. Andry, B. Dang, R. R. Horton, C. S. Patel, R. J. Polastre, K. Sakuma, E. S. Sprogis, C. K. Tsang, B. C. Webb and S. L. Wright: *Proc. 58th Electronic Components and Technology Conf.*, (Lake Buena Vista, Florida, 2008) pp. 538–543.
- 7) S. J. Koester, A. M. Young, R. R. Yu, S. Purushothaman, K. N. Chen, D. C. La Tulipe, Jr., N. Rana, L. Shi, M. R. Wordeman and E. J. Sprogis: *IBM J. Res. Dev.* **52** (2008) 583–597.
- 8) E. Higurashi, D. Chino, T. Suga and R. Sawada: *IEEE J. Sel. Top. Quantum Electron.* **15** (2009) 1500–1505.
- 9) S. Tukiya, T. Sugimoto and Y. Ohno: *Proc. 7th IEEE Electronics Packaging Technology Conf.*, (Singapore, 2005) pp. 792–796.
- 10) Y. H. Wang and T. Suga: *Proc. 58th Electronic Components and Technology Conf.*, (Lake Buena Vista, Florida, 2008) pp. 944–949.
- 11) N. Unami, K. Sakuma, J. Mizuno and S. Shoji: *Jpn. J. Appl. Phys.* **49** (2010) 06GN12.