ISSN 0020-1685, Inorganic Materials, 2009, Vol. 45, No. 4, pp. 343–346. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © D.I. Brinkevich, S.A. Vabishchevich, N.V. Vabishchevich, V.S. Prosolovich, 2009, published in Neorganicheskie Materialy, 2009, Vol. 45, No. 4, pp. 389–392.

Strength Degradation of Silicon Diffusion-Doped with Gold

D. I. Brinkevich[a], S. A. Vabishchevich[b], N. V. Vabishchevich[b], and V. S. Prosolovich[a]

[a] *Belarussian State University, pr. Nezavisimosti 4, Minsk 220030, Belarus*
[b] *Polotsk State University, ul. Blokhina 29, Novopolotsk, 211440 Belarus*
e-mail: brinkevich@bsu.by

Received January 24, 2008

Abstract—Diffusion doping with gold is shown to reduce the microhardness of silicon single crystals. Oxygen precipitation suppresses this process because diffusing interstitial gold atoms, Au_i, interact with oxygen and become captured by growing precipitates.

DOI: 10.1134/S0020168509040013

INTRODUCTION

Silicon is the basic material of modern microelectronics. In addition, it is a key component in the fabrication of sensors, micro- and nanoelectromechanical systems, and other hybrid nanodevices. In this context, the study of the influence of various processing steps on its mechanical properties (Young's modulus, hardness, wear resistance, and others) is of special importance.

Gold doping is widely used to reduce the carrier lifetime in silicon and, accordingly, to enhance the speed of semiconductor devices [1]. Gold-doped silicon is the key material for high-sensitivity IR detectors [2]. Its strength, however, is essentially unexplored. Such studies are of high current interest because, in subsequent steps of semiconductor device fabrication (oxidation, diffusion, chip bonding, and others), silicon wafers are exposed to thermal and mechanical influences, which give rise to buckling and microcracking of the wafers. These processes reduce the yield of devices to specification and are determined in large part by the strength of the implanted wafers.

The objective of this work was to study the effect of Au diffusion doping on the microhardness of silicon.

EXPERIMENTAL

Silicon wafers were prepared from Czochralski-grown ingots. In our experiments, we used dislocation-free KEF-20 (phosphorus-doped, nominal resistivity of 20 Ω cm) silicon wafers differing in oxygen concentration (table). The interstitial oxygen concentration was evaluated from the strength of the 1106-cm^{-1} absorption band. The dislocation density was determined using selective etching and was within 10^2 cm^{-2} in all of our samples.

Microhardness H was measured in the [100] direction by a standard technique using a PMT-3 tester fitted with a square-pyramidal diamond indenter tip with an apical angle of 136°. The indentation load was varied from 0.5 to 2 N.

The choice of the load was dictated by two factors:

1. The indent depth must be sufficiently large to rule out surface effects.

2. Indentation must produce no cracks.

At a 0.50-N load, the indent depth was ~1μm, which minimized the effect of surface processing. At the highest load, the fraction of cracked indents, unsuitable for H determination, was within 10%. In each experiment, at least 50 indents were placed on the wafer surface. We measured the two indent diagonals, and the average was used to determine H [3].

The results were analyzed using statistical methods [4]. The microhardness data were found to follow a normal (Gaussian) distribution. The uncertainty in our H measurements was 2% (at a 95% confidence level).

As a gold diffusion source, we used a film produced on the surface of a 2-mm-thick silicon wafer by chemical deposition from a potassium dicyanoaurate solution. Diffusions were carried out in a hydrogen atmosphere at 925°C over a period of 5 h. Next, the surface

Effect of heat treatment at 925°C for 5 h on the interstitial oxygen concentration in silicon

Sample no.	$N_O \times 10^{-17}$, cm^{-3}			$N_{Au} \times 10^{-14}$, cm^{-3}
	as-prepared	heat-treated	Au-diffused	
1	6.9	6.9	6.9	3.1
2	8.9	8.2	9.8	5.3
3	9.6	5.9	4.0	7.0
4	10.1	4.0	2.8	9.5

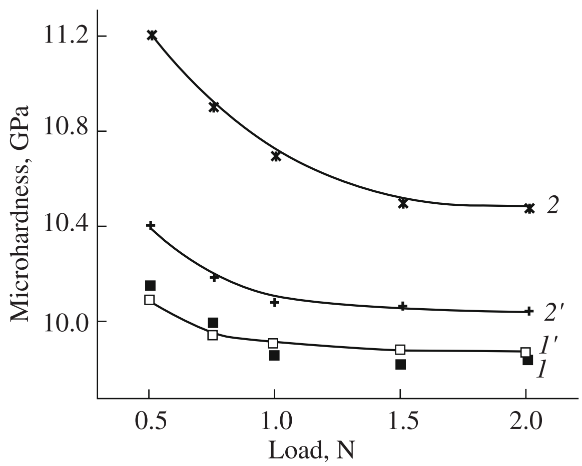

Fig. 1. Microhardness as a function of indentation load for (*1*, *1*') as-prepared and (*2*, *2*') heat-treated silicon wafers at oxygen concentrations of (*1*, *2*) 6.9×10^{17} and (*1*, *2*) 10.1×10^{17} cm^{-3}.

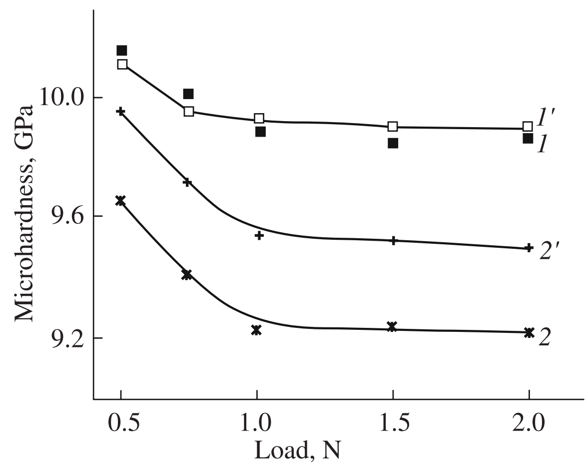

Fig. 2. Microhardness as a function of indentation load for (*1*, *1*') as-prepared and (*2*, *2*') gold-diffused silicon wafers at oxygen concentrations of (*1*, *2*) 6.9×10^{17} and (*1*, *2*) 10.1×10^{17} cm^{-3}.

damage layer up to 100 μm in thickness was ground away, and the wafer surface was polished.

The gold concentration in the samples was determined by neutron activation analysis (table). A number of samples (controls) were heat-treated under the same conditions without gold diffusion. The Au impurity concentration in those samples was insensitive to heat treatment and was close to that in the as-prepared wafers (~5×10^{12} cm^{-3}). The electroactive gold concentration was inferred from Hall effect measurements by a standard technique at temperatures from 78 to 300 K in dc electric and magnetic fields [5].

RESULTS AND DISCUSSION

The microhardness of the as-grown silicon single crystals was about 9.8 GPa (at a 1-N load) and depended very little on the oxygen concentration in the range $N_O = (6.9–10.1) \times 10^{17}$ cm^{-3} (Fig. 1). The plots of microhardness versus indentation load for all of our samples are typical of nonplastic (hard) crystals (Figs. 1, 2): increasing the load from 0.5 to 1 N reduces the microhardness; at higher loads, H varies insignificantly. According to Gerasimov et al. [6], the increased hardness in the surface layer of silicon single crystals is due to bond dimerization on the semiconductor surface and the development of surface microroughness.

Gold diffusion was found to reduce the microhardness of the silicon single crystals (Fig. 2). The strength loss was less pronounced at higher oxygen concentrations (Fig. 2, curves *2*, *2*'). At the same time, heat treatment at 925°C for 5 h with no gold diffusion increased the microhardness of control samples (Fig. 1, curves *2*, *2*'). A similar effect was observed earlier at lower annealing temperatures, 150–800°C [7, 8]. The change in microhardness in our experiments (2–5%) was smaller than that at 800°C (~8% [8]) but exceeded that produced by low-temperature (150°C) annealing (1.5–2%) [7].

Heat treatment of control samples with interstitial oxygen concentrations above 8×10^{17} cm^{-3} led to active oxygen precipitation (table) [9]. The process was substantially more effective at higher interstitial oxygen concentrations: at $N_O = 10.1 \times 10^{17}$ cm^{-3}, the fraction of precipitated oxygen reached ~75%. At $N_O = 6.9 \times 10^{17}$ cm^{-3}, heat treatment had little or no effect on the interstitial oxygen concentration (table). Note that, in the case of active oxygen precipitation, the increase in H was smaller (Fig. 1, curve *2*'). Thus, we are led to conclude that oxygen precipitation reduces the microhardness of silicon.

The present experimental data can be interpreted as follows: Heat treatment of single-crystal silicon near 900°C leads to a transformation of *B*-defects—aggregates of silicon self-interstitials, Si_i, stabilized by carbon atoms [10], which are capable of forming interstitial-type point defects (and/or defect complexes), thereby raising the strength of the crystal [11]. Heating causes *B*-defects to emit self-interstitials. The liberated carbon atoms, which have a smaller covalent radius (0.77 Å [11]) compared to Si atoms (1.17 Å [12]), compress the silicon lattice, thereby reducing the bond length and, accordingly, raising the strength of the crystal. These processes seem to be responsible for the observed influence of heat treatment on the hardness of silicon.

Oxygen impurities also have a significant effect on the mechanical properties of single-crystal silicon. Oxygen atoms in silicon are known [13] to impede dislocation propagation and multiplication during deformation and must, therefore, increase the strength of the material. The hardening effect of interstitial oxygen is also evidenced by the fact that the microhardness of oxygen-free float-zone silicon is substantially (5–10%)

lower than that of Czochralski Si. Thus, oxygen precipitation, accompanied by the removal of oxygen atoms from interstitial positions, must reduce the strength of silicon single crystals. Moreover, oxygen precipitation is accompanied by generation of self-interstitials [14], which would be expected to assist in suppressing the above-mentioned transformation of *B*-defects during heating and, accordingly, to reduce the microhardness.

Thus, two competing processes influence the variation in the microhardness of oxygen-containing Si during heat treatment: oxygen precipitation, which reduces the microhardness of the material, and the transformation of *B*-defects, accompanied by the formation of interstitial-type defects, which raises the microhardness of silicon. Our experimental data indicate that the latter process prevails.

Gold diffusion produces marked changes in the mechanical properties of single-crystal silicon. There are several reasons for this. In *n*-type silicon, compensating gold acceptor centers have the form of negatively charged atoms on lattice sites, Au_s [9]. Gold atoms diffuse into silicon through interstices and occupy electroactive, substitutional positions by kicking out Si atoms into interstices [15]:

$$Au_i \longleftrightarrow Au_s + Si_i.$$

As pointed out above, the Si_i self-interstitials created by substitutional gold atoms must raise the strength of silicon. However, at high supersaturations with self-interstitials, as is the case with gold diffusion, *B*-defects capture Si_i and grow to small interstitial-type dislocation loops, referred to as *A*-defects [10, 16]. *A*-defects are effective traps for interstitial atoms. They eliminate supersaturation with Si_i and cause interstitial point defects to decompose, thereby reducing the strength of Si single crystals.

Moreover, substitutional Au atoms, whose radius (1.44 Å [12]) considerably exceeds that of Si atoms (1.17 Å [12]), expand the silicon lattice, increasing the bond length and, accordingly, reducing the microhardness of the crystal. A similar strength loss under the effect of compressive strain was reported earlier for a number of electroinactive impurities in silicon: germanium [8], tin [17], and rare-earth elements [18].

Au_i atoms diffusing in Czochralski silicon effectively interact with oxygen [9, 19, 20] and become captured by precipitates growing during heat treatment, without occupying electroactive, substitutional positions. In particular, in this study most of the gold atoms (>90%) in silicon with $N_O = 10.1 \times 10^{17}$ cm^{-3} were electroinactive and, hence, did not reside in substitutional sites. During gold diffusion in silicon with a high interstitial oxygen concentration, this should prevent strength degradation.

CONCLUSIONS

Diffusion doping with gold was shown to reduce the microhardness of silicon single crystals. Oxygen precipitation suppresses this process because diffusing gold atoms, Au_i, interact with oxygen and become captured by growing precipitates.

REFERENCES

1. Ravi, K.V., *Imperfections and Impurities in Semiconductor Silicon*, New York: Wiley, 1981.
2. Mil'vidskii, M.G., *Poluprovodnikovye materialy v sovremennoi elektronike* (Semiconductor Materials in Modern Electronics), Moscow: Nauka, 1986.
3. Berezina, G.M., Microhardness Measurements in Silicon, *Dokl. Akad. Nauk BSSR*, 1979, vol. 33, no. 5, pp. 431–433.
4. Kalosha, V.K., Lobko, S.I., and Chikova, T.S., *Matematicheskaya obrabotka rezul'tatov eksperimenta* (Mathematical Methods for Data Processing), Minsk: Vysshaya Shkola, 1982.
5. Kuchis, E.V., *Gal'vanomagnitnye effekty i metody ikh issledovaniya* (Galvanomagnetic Effects and Methods for Their Investigation), Moscow: Radio i Svyaz', 1990.
6. Gerasimov, A.B., Chiradze, G.D., Kazarov, R.E., et al., Physical Nature of Microhardness Variations with Depth, *Fiz. Khim. Obrab. Mater.*, 2004, no. 3, pp. 71–74.
7. Berezina, G.M., Korshunov, F.P., and Murin, L.I., Effect of Low-Temperature Annealing on the Microhardness of Silicon, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1990, vol. 26, no. 4, pp. 683–686.
8. Brinkevich, D.I., Vabishchevich, S.A., and Petrov, V.V., Effect of Group IIIB and IV Impurities on the Microhardness of Single-Crystal Silicon, *Mikroelektronika*, 1997, vol. 26, no. 4, pp. 297–300.
9. Brinkevich, D.I., Kryukov, V.L., Meraai, F., et al., The Effect of Oxygen on the Behavior of Gold Impurities in Silicon, *Neorg. Mater.*, 1993, vol. 29, no. 12, pp. 1587–1589 [*Inorg. Mater.* (Engl. Transl.), vol. 29, no. 12, pp. 1421–1423].
10. Vysotskaya, V.V., Gorin, S.N., and Sidorov, Yu.A., On the Nature of *B*-Defects in Silicon, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1990, vol. 26, no. 3, pp. 453–457.
11. Golovin, Yu.I., Dmitrievskii, A.A., and Suchkova, N.Yu., Structure of Complexes Responsible for Radiation-Induced Strength Degradation of Silicon, *Fiz. Tverd. Tela* (S.-Peterburg), 2006, vol. 48, no. 2, pp. 262–265.
12. *Fiziko-khimicheskie svoistva elementov: Spravochnik* (Physicochemical Properties of Elements: A Handbook), Samsonov, G.V., Ed., Kiev: Naukova Dumka, 1965.
13. Sumino, K., Interaction of Dislocation with Impurities and Influence on the Mechanical Properties of Silicon Crystals, *Symp. Defects in Semiconductors*, Boston, 1982, pp. 307–321.
14. Vigdorovich, V.N., Kryukov, V.L., and Furmanov, G.P., Relationship between Gold Diffusion and Oxygen Precipitation in Silicon, *Dokl. Akad. Nauk SSSR*, 1991, vol. 317, no. 2, pp. 359–363.
15. Aleksandrov, O.V. and Krivoruchko, A.A., Impurity Outdiffusion by the Kick-Out Mechanism during Getter-

ing, *Fiz. Tekh. Poluprovodn.* (S.-Peterburg), 2007, vol. 41, no. 9, pp. 1066–1073.

16. Seeger, A., Föll, H., and Frank, W., Self-Interstitials, Vacancies, and Their Aggregates in Silicon and Germanium, *Point Defects in Solids*, Crawford, J.H. and Slifkin, L.M., Eds., New York: Plenum, 1975.
17. Brinkevich, D.I., Vabishchevich, S.A., and Prosolovich, V.S., Microhardness of Silicon Layers Grown by Liquid Phase Epitaxy, *Neorg. Mater.*, 2007, vol. 43, no. 10, pp. 1159–1163 [*Inorg. Mater.* (Engl. Transl.), vol. 43, no. 10, pp. 1035–1039].
18. Brinkevich, D.I., Vabishchevich, S.A., and Prosolovich, V.S., A Mechanism Underlying the Effect of Nd on the Strength of Silicon Single Crystals, *Perspekt. Mater.*, 2007, no. 7, pp. 31–34.
19. Lang, D.V., Grimmeiss, H.G., Meijer, E., and Jaros, M., Complex Nature of Gold-Related Deep Levels in Silicon, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1980, vol. 22, no. 7, pp. 3917–3934.
20. Bykovskii, Yu.A., Voronkova, G.M., Grigor'ev, V.V., et al., Effect of Preannealing on Substitutional Gold Concentration in Silicon, *Neorg. Mater.*, 2002, vol. 38, no. 6, pp. 647–658 [*Inorg. Mater.* (Engl. Transl.), vol. 38, no. 6, pp. 529–538].