Si Kα Chemical Shift and Charge State of Si in Metal Silicides

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By measuring high-resolution Si Kα x-ray fluorescence spectra, chemical shifts and effective charges of Si in both magnesium (Mg_2Si) and calcium silicides (CaSi) have been investigated. CaSi showed a small but positive chemical shifts (+0.03 eV) while chemical shift of Mg_2Si was negative (-0.14 eV) as expected from their electronegativity (Ca: 1.00, Mg: 1.31, Si: 1.90). The similarity of Fe silicides and calculations for free-single Si atom suggested that the effective charge of Si for CaSi was positive. The present study shows agreement with the conventional understanding for the Si charges in Mg sillicide but is completely opposite for Ca silicides, as reported for Fe silicides.

INTRODUCTION

The effective charge is useful to understand the chemical bond between silicon and neighboring metal atoms in metal silicides. A practical parameter to determine the effective charge of binary compounds is the electronegativity proposed by Mulliken [1] or Pauling [2, 3]. The electronegativity of Si is 1.90; metal electronegativities are 1.66 for Cr, 1.55 for Mn, 1.83 for Fe, 1.88 for Co, 1.91 for Ni, 1.90 for Cu, 1.31 for Mg and 1.00 for Ca [4,5]. Since the electronegativity defined by Pauling is "the power of an atom in a molecule to attract electrons to itself", the effective charge is clearly defined when we apply the electronegativity to an H_2S molecule or an SiF_6^{2-} cluster. However for solids, it is sometimes difficult to apply the electronegativity to define the effective charge of each atom. This is because the electronegativity is at least a good parameter to determine whether each atom is either positively charged or not, depending on the neighbor atoms. Based on the difference of electronegativities, the effective charge on Si in most of the silicides except for Ni are negative values; metal is positively charged, and silicon is negatively charged. For nickel silicides, Xu *et al.* [6] calculated the charge transfer of Ni_3Si and $NiSi_2$ using the self-consistent LMTO method. Their results showed that 0.1 electrons were transferred from two Si atoms to a Ni atom for $NiSi_2$, and 0.03 for Ni_3Si. The total number of electrons within the Ni sphere increased but the Ni *d* electrons decreased. The overall effective charge on Si atom in nickel silicides is positive, which is in good agreement with that estimated from the electronegativity of nickel; the electronegativity of Ni is slightly larger than silicon defined by Mulliken and Pauling. However, recently some of the present authors [7] measured the chemical shift of Si $Kα_{1,2}$ x-ray lines for iron silicides, and found that silicon was positively charged, in spite that the electronegativity of silicon is larger than that of iron. The characteristic X-ray emission lines $Kα_{1,2}$ are emitted from a core hole transition from $1s^{-1}$ to $2p^{-1}$. The chemical shift is strongly correlated to the effective charge of the X-ray emitting atom [8-10]. Leonhardt *et al.* [8] calculated chemical shifts of Kα for elements of the third period according to the free-ion model and presented the dependence on the effective charges: the chemical shift was positive when the atom was charged positive whereas shift was negative for the negatively charged atom. Petrovitch *et al.* [11] also pointed out that a smaller effective number of electrons in the valence band shifts the inner-shell electrons to higher binding energy which cause a higher energy for the Kα

emission line. As increasing the effective charges, the Kα$_{1,2}$ line (K-L$_{3,2}$) shifted to higher energy. The electronegativity of neighbor atoms changed effective charges on Si atoms and caused the chemical shift. Comparison with the chemical shift and the effective charge enables us to identify the chemical state of the atoms in unknown compounds not only qualitatively but also quantitatively [12].

Thus, positive shifts of Si atoms in Fe silicides seemed somewhat strange because electronegativity of Si was larger than that of Fe. To elucidate chemical bonding in metal silicides, we investigated the chemical shifts and the effective charges of Si in Ca and Mg silicides, where electronegativity of Ca and Mg were much smaller than that of Si. We measured the Si Kα x-ray fluorescence spectra of Mg$_2$Si and CaSi. We also investigated the sample position effect in high resolution x-ray fluorescence measurements. In this paper, we will present the positive charge of Si atoms in calcium silicides while Si atoms in Mg$_2$Si had negative effective charge.

EXPERIMENTAL

High resolution Si Kα x-ray fluorescence spectra were measured on a double crystal vacuum x-ray fluorescence spectrometer (Rigaku, Japan). A W-anode tube was operated at 35 kV and 20 mA as an excitation source. Si-Kα x-rays were monochromatized by using two InSb(111) (2d=0.74806 nm) crystals and detected with a flow proportional counter. Details of instrumental setup have been described elsewhere [13]. Measured Mg$_2$Si sample was slugs. Powder specimens (CaSi) were pressed into briquettes. A Si wafer was used as a reference. The x-ray fluorescence spectra were recorded in a stepwise mode with a step of 0.01° in 2θ, i.e. 0.05 eV at 1740 eV. Before and after each sample measurement, we measured the spectra of pure Si to check the reproducibility and calibrated the energy shift (±0.01 eV) of monocromators due to the change of the temperature. The Si Kα spectra of calcium silicides were also measured by using two ADP(101) (ammonium dihydrogen phosphate: NH$_4$PO$_4$, 2d=1.0640 nm) crystals. The spectra were plotted in energy scale.
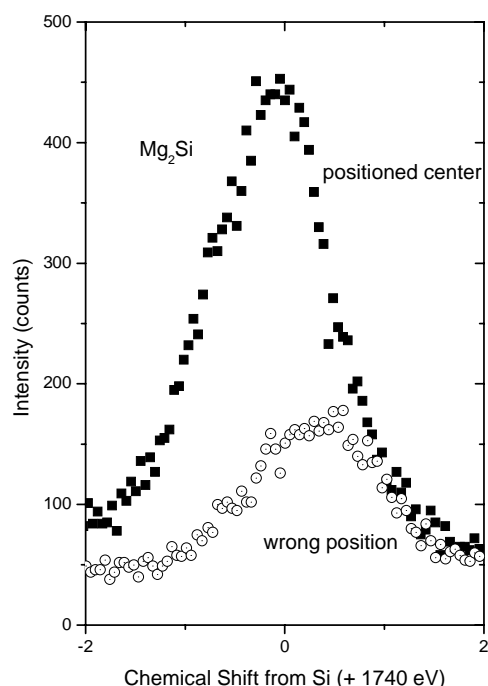

Fig.1 The sample position effect in Si Kα x-ray fluorescence spectra of a small Mg$_2$Si specimen. Closed squares: measured at the center of the analysis area. Open circles: 10 mm off-center position.

RESULTS AND DISCUSSION

In order to measure chemical shifts precisely, we firstly investigate the sample position effect in the high resolution fluoresce x-ray measurements. We measured Si Kα X-ray fluorescence spectra of a smaller Mg$_2$Si slug, which measurement area for the analysis was about 10×20 mm^2, with changing the sample position: positioned at the center and off center with the distance of about 10 mm. Typical measurement area of specimens in this instrument was the circle with the diameter of 32 – 38 mm φ. Both raw experimental Si Kα x-ray fluorescence spectra of Mg$_2$Si are shown in Fig. 1. The specimen positioned at the center gave more intense Si Kα spectrum with the negative chemical shift. On the contrary, the x-ray fluorescence spectrum from the off-center sample was not only weaker but also shifted to much higher energy. This is because the incident angle of detected x-ray to the first monochromator was changed as the sample position was changed. Since the measurement sample areas were enough larger, 38 mm φ for Si and 32 mm φ for
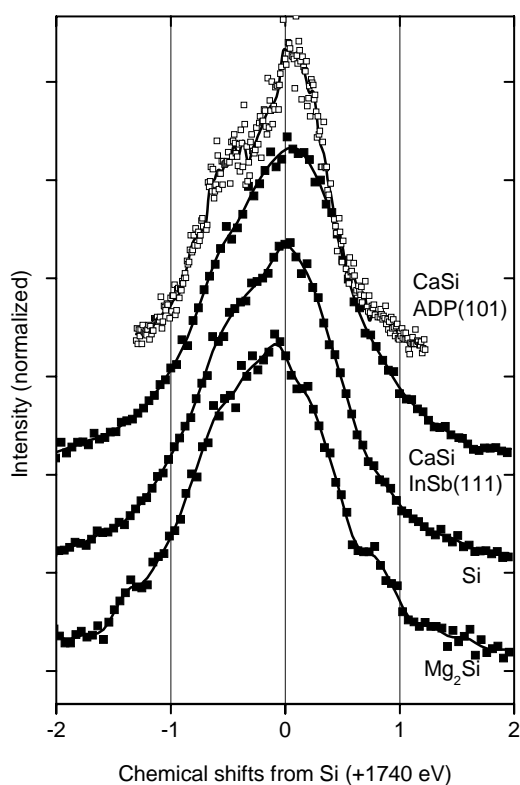
Fig. 2 The Si Kα x-ray fluorescence spectra of Mg and Ca silicides. Dot: the raw experimental data. Solid line: after Savitzky-Golay smoothing, which parameters are given in text.

Table 1. Chemical shifts for Si Kα lines of Mg and Ca silicides.

Samples	Measured chemical shifts for Si Kα lines (eV)
Mg$_2$Si	-0.14±0.02
CaSi (InSb(111))	+0.03±0.02
CaSi (ADP(101))	+0.03±0.02

CaSi, the sample position effect was negligible for these samples. Thus, in order to measured chemical shifts of Si Kα spectra precisely, i.e. ±0.02 eV precision, a lager sample should be measured at the center of the analysis area. For high resolution measurements we used 3 slugs as Mg$_2$Si sample, which measurement area was about 30 mm φ. Thus we could neglect the sample position effects in the following measurements.

The Si Kα x-ray fluorescence spectra of Si, Mg$_2$Si and CaSi are shown in Fig. 2 after normalization with respect to peak maximum. The measured spectra were numerically smoothed 10 times by a least squares method of Savitzky and Golay [14-16] (second order, seven points). The chemical shifts in Table 1 were defined as the energy change of Si Kα doublets. Here, we use the center energy of full width at 9/10 of Kα peak maxima [17]. Si Kα spectra of Mg$_2$Si shifted to lower energy (-0.14

eV) while the chemical shift of Si Kα spectra in CaSi was small but positive (+0.03 eV). As mentioned above, the error for the determination of the peak position was 0.01 eV, so the error of the chemical shift was estimated to be 0.02 eV. For the comparison with the chemical shifts of other silicon compounds and Fe silicides measured in ref. 7, we also measured the Si Kα spectrum of CaSi with ADP crystals. In spite of the lower signal, positive chemical shift of +0.03 eV was also detected and almost same to that measured with InSb(111) crystals. In general, the direction of chemical shifts is related to the effective charge of the concerning atom. The chemical shifts of Si Kα and the effective charges of Si atoms showed a good correlation when the neighbor atom of Si went from B to F [7]. This leads a result that Si atoms of CaSi would be positively charged while effective charge of Si in Mg$_2$Si was negative. On the contrary, electronegativity of these elements increase in the sequence of Ca<Mg<Si (Ca: 1.00, Mg: 1.31, Si: 1.90, defined by Pauling [2,5]). This suggests Si atoms in these silicides are all negatively charged.

To elucidate this contradiction, we calculated the effective charges and the chemical shift of Si Ka for a free single Si atom by using the discrete variational (DV) Hatree-Fock-Slater (Xα) method [18-20]. As shown in Table 2, chemical shift is negative when Si had a negative charge while a positive charge induced a positive shift. From this point of view, it could be concluded that Si in CaSi is positively charged whereas the effective charge of Si of Mg$_2$Si is negative. On the contrary, Kawai *et al.* [17, 21] pointed out that chemical shifts of Kα lines for 3d transition metals showed the opposite peak shifts whether the ionization of electrons occurred from the 3d orbital or the 4s orbital. For Ti$^+$, the 3d^{2}4s^1 state induces a positive chemical shift while the 3d^{1}4s^2

Table 2 DV-Xα calculations of chemical shift of free single Si atom.

Si valence state	$3s^23p^1$	$3s^23p^2$	$3s^23p^3$	$3s^23p^23d^1$
Total charge (electrons per Si atoms)	+1	0	-1	-1
Si 2p (eV)	-99.68	-85.88	-73.00	-74.24
Si 1s (eV)	-1780.33	-1765.92	-1752.57	-1754.59
Si 2p – Si 1s (eV)	1680.65	1680.04	1679.57	1680.35
Chemical shifts (eV)	0.61	0.00	-0.47	0.31

ionization shows a negative shift even if the effective charge of Ti is same. For CaSi, if back bonding from Ca atoms to the Si atom occurred, Si 3d orbital would be occupied. As shown in Table 2, the DV-Xα calculation for a free Si atom with minus charge (-1 electron) also indicated the plus chemical shift (+0.31 eV) for Si- when one electron occupied the 3d state. Thus, two possible causes for the plus chemical shift of CaSi were considerable: i) plus charge on Si, ii) minus charge on Si with Si 3d contribution to Ca-Si bonding.

However, the energy of the 3d orbital energy of Si is usually sufficiently high enough in the unoccupied continuum level. Chemical bonds of transition metal silicides have been generally described in terms of the hybridization between metal d and silicon p state [22, 23]. The bonding in calcium silicides has been also explained as a general hybridization between Ca s-p-d and Si s-p states [24]. Thus, we can neglect the role of Si 3d orbital in Ca-Si chemical bonding. Si in CaSi should be considered as a positively charged atom. Liu *et al.* [7] measured Si K spectra of both FeSi and $FeSi_2$ and concluded that Si had positive charges whereas the relative electronegativity of Fe and Si were 1.83 and 1.90, respectively. The similarity of Fe-Si bi-systems supported the conclusion that the small positive charge existed in Si atoms of CaSi. Thus it is concluded that positive charge on Si causes the small positives chemical shift of Si Kα spectra for CaSi.

While calcium silicides can be formed as Ca_2Si, CaSi and $CaSi_2$, Mg_2Si is the only possible stoichiometry for magnesium silicides [25]. Every Si atom is surrounded by eight nearest neighbor Mg atoms. Thus, the electron transfer from Mg to Si may easily occur. Si 2p XPS results for Mg_2Si on Si(100) [26] and Si(111) [27] also showed the negative chemical shifts. The results presented in this paper for Mg_2Si agreed with these XPS studies and the ordinary understanding for the charge state of Si. The nearest neighbor atoms in both silicides induced this difference of effective charges between CaSi and Mg_2Si although electronegativity of Ca and Mg is smaller than that of Si.

CONCLUSION

Chemical bonding of Mg_2Si and CaSi have been investigated from Si Kα x-ray fluorescence spectra measured by using a high resolution double crystal fluorescence spectrometer. Although both electronegativity of Mg (1.31) and Ca (1.00) were smaller than that of Si (1.90), chemical bonding in both Mg and Ca silicides shows different behaviors. Negative chemical shift of Si Kα in Mg_2Si showed that effective charge of Si was negative as expected from electronegativity. On the contrary, a small but positive chemical shift in CaSi suggested the Si was positively charged as Fe silicides (FeSi and $FeSi_2$) although electronegativity of Ca is smaller than Mg and Si. The present study shows agreement with the conventional understanding for the Si charges in Mg sillicide but is completely opposite for Ca silicides, as reported for Fe silicides.

REFERENCES
[1] R. S. Mulliken, J. Chem. Phys., **2**, 782 (1934).

[2] L. Pauling, J. Am. Chem. Soc., **54**, 3570 (1932).

[3] L. Pauling, "The Nature of Chemical Bond", 3rd ed, pp.88-98 (Cornell Univ. Press, New York, 1960).

[4] F. A. Cotton, and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed. p.103 (Wiley, New York 1972).

[5] A. L. Allred, J. Inorg. Nucl. Chem., **17**, 215 (1961).

[6] J. -H. Xu, and Y.-N.Xu, Solid State Commun., **55**, 891 (1985).

[7] Z. Liu, S. Sugata, K. Yuge, M. Nagasono, K. Tanaka, and J. Kawai, Phys. Rev., **B69**, 035106 (2004).

[8] G. Leonhardt, and A. Meisel, J. Chem. Phys., **52**, 6189 (1970).

[9] A. Meisel, G. Leonhardt, and R. Szargan, "X-ray Spectra and Chemical Bonding" (Springer-Verlag, Berlin, 1989).

[10] W. L. Baun and D. W. Fisher, Spectrochim. Acta, **21**, 1471 (1965).

[11] E. V.Pettrovich, Yu. P. Smimov, V. S. Zykov, A. I. Grushko, O. L. Sumbaev, I. M. Band, and M. B. Trzhaskovskaya, Zh. Éksp. Teor. Fiz., **61**, 1756 (1971) [Sov. Phys. JETP **34**, 935 (1972)].

[12] Y. Gohshi and A. Ohtuka, Spectrochim. Acta, Part **B 28**, 179 (1973).

[13] Y. Gohshi, H. Kamada, K. Kohra, T. Utaka, and T. Arai, Appl. Spectrosc., **36**, 171 (1982).

[14] A. Savitzky and M. J. E. Golay, Anal. Chem., **36**, 16207 (1964).

[15] A. Proctor and P. M. A. Sherwood, Anal. Chem., **52**, 2315 (1980).

[16] J. Steiner, Y. Termonia, and J. Deiou, Anal.Chem., **44**, 1990 (1972).

[17] J. Kawai, E. Nakamura, Y. Nihei, K. Fujisawa, and Y. Gohshi, Spectrochim. Acta, **45B**, 463 (1990).

[18] H. Adachi, M. Tsukuda, and C. Satoko, J. Phys. Soc. Jpn., **45**, 1528 (1978).

[19] C. Satoko, M. Tsukada, and H. Adachi, J. Phys. Soc. Jpn., **45** 1333 (1978).

[20] H. Adachi, S. Shiokawa, M. Tsukuda, C. Satoko, and S. Sugano, J. Phys. Soc. Jpn., **47**, 1528 (1979).

[21] J. Kawai, T. Konishi, A. Shinohara, and Y. Gohshi, Spectrochim. Acta., **49B**, 725, 1994.

[22] P. S. Ho, G. W. Rubloff, J. E. Lewis, V. L. Moruzzi, and A. R. Williams, Phys Rev., **B 22**, 4784 (1980).

[23] O. Bisi, and C. Calandra, J. Phys., C **14**, 5479 (1981).

[24] O. Bisi, L. Braicovich, C.Carbone, I. Lindau, A. Iandelli, G. L. Olcese, and A. Palenzona, Phys. Rev., **B 40**, 10194 (1989).

[25] C. J. Smithells, "Metals Reference Book", 5th ed. (Butterworths, London, 1976).

[26] M. R. J. van Buuren, F. Voermans, and H. van Kempen, J. Phys. Chem., **99**, 9519 (1995).

[27] M. Brause, B. Braun, D. Ochs, W. Mau-Friedrichs, and V. Kempter, Surface Sci., **398**, 184 (1998).