DETERMINATION OF RELATIVE TRANSITION PROBABILITIES FOR THE Si I AND Si II LINES OF SILICON

By W. Żyrnicki, A. Czernichowski

And W. Mleczko

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław*

The authors analyzed the emission spectrum of plasma (argonium with some $SiCl_4$ added) generated in a plasmatron. The intensities of Si I and Si II lines were used for calculating relative transition probabilities [1]. The temperature of the plasma was determined by the one spectral line method, using the argonium Ar I lines for which the transition probabilities are known. The paper gives relative probabilities for 27 Si I lines and 5 Si II lines in the UV and violet regions. The results obtained are compared with those obtained by other authors.

Introduction

Owing to the abundance of silicon in nature it is very important to possess knowledge of the accurate transition probabilities of its spectral lines. This paper presents our studies in the UV and violet regions where experimental values of the transition probabilities for many silicon lines are unknown or the data are inaccurate. The results obtained by various authors from theoretical calculations or semi-empirical and empirical methods differ sometimes even in their order of magnitude.

Theoretical part

The spectral line recorded in the photographic emulsion placed in a spectrograph is formed as a result of a proper emission act occurring in many atoms or ions. The intensity I of such a line (usually $erg/cm^3 \cdot sec \cdot srd$) is a function of several factors which may be presented by the equation

$$I = \frac{1}{4\pi} \cdot N \cdot \frac{g_n}{Q(T)} \cdot \exp\left(-\frac{E_n}{kT}\right) \cdot A_{nm} \cdot h \cdot \nu_{nm}. \tag{2}$$

Since the spectral line has a certain width, the left-hand member of equation (1) will be an integral $\int_{\lambda'}^{\lambda''} I(\lambda)d\lambda \cdot A_{nm}$ is Einstein's probability of spontaneous emission due to an electron transition from a higher energy level n to a lower one m, N is the number of atoms (ions) in 1 cm^3, g_n is the statistical weight of the higher level, E_n is the excited level energy, k is the Boltzman constant, T is the absolute temperature, $Q(T)$ is the electron energy distribution function, ν_{nm} is the frequency corresponding to the $n-m$ transition, and λ is the wavelength of the spectral line, whose width is $\lambda'-\lambda''$.

Equation (1) is valid for optically thin layers, such as the layers analyzed by the authors, and is satisfied only if a local thermodynamic equilibrium (LTE) exists.

On the basis of equation (1) the relative transition probability for two lines of an atom or ion may be expressed by the equation

$$
\frac{A_{nm}^{(1)}}{A_{nm}^{(2)}} = \frac{\int_{\lambda'}^{\lambda''} I^{(1)}(\lambda)d\lambda \cdot g_n^{(2)} \cdot \nu_{nm}^{(2)}}{\int_{\lambda'}^{\lambda''} I^{(2)}(\lambda)d\lambda \cdot g_n^{(1)} \cdot \nu_{nm}^{(1)}} \exp \frac{E_n^{(1)}-E_n^{(2)}}{kT} \cdot \tag{2}
$$

Apparatus and measurements

The excitation source was a plasma jet with copper anode and tungsten cathode, 2% ThO$_2$ added, operating in an atmosphere of pure argon. The jet load was variable from 12 to 14 kW. The diameter of the anodic outlet duct was 8 mm. The anode was adapted for introducing an additional stream of argon, saturated with SiCl$_4$ vapors, beyond the arc space. This was to avoid electrode erosion by SiCl$_4$ vapors and to ensure stable operation of the jet.

The rates of the main (8 Nl/min) and additional (1.5 or 1.0 Nl/min) streams of argon were controlled by means of calibrated rotameters. The vessel containing SiCl$_4$ was thermostatted at 0°C.

A horizontal stream of plasma, protected against contact with the atmosphere by means of a chamber with quartz windows, was calibrated on the spectrograph slit with the help of an achromatic quartz lens. The photographs were made in a Zeiss PGS-2 grating spectrograph at a resolution of 7.37 Å/mm. The spectra were recorded on Orwo UV-1 plates.

As light sources of known energy distributions, the authors employed a tape tungsten lamp of an actual temperature 2800°K (3800–4400 Å) and a standard carbon arc of a temperature of 3792°K (2200–3000 Å) [2].

The density calibration curve of the photographic emulsion was made by means of an iron arc whose spectrum was recorded in the plate through a three-stage attenuator.

The light calibration system for the spectra of iron, the carbon arc, tungsten lamp and plasma was the same.

Moreover, the spectra of the plasma, iron and carbon arc (lamp) were recorded on the same plate.

The photographs were analyzed by means of a Zeiss G II microphotometer with a G1B1 recorder.

Calculations

The density profile of a given spectral line recorded with the microphotometer was converted by means of an emulsion density curve into the function of line intensity and wavelength. Then, the surface area under the resulting curve was calculated. The obtained value of $I(x)$ was the sum of intensities $I(r)$ for layers surrounding the axis of plasma stream perpendicularly to the recording plate. The value $I(x)$ and the required value $I(r) = \int_{\lambda'}^{\lambda''} I(\lambda) d\lambda$ are interrelated by the known Abel equation

$$I(x) = 2 \int_{x}^{R} \frac{I(r) \cdot r \cdot dr}{\sqrt{r^2 - x^2}} \tag{3}$$

which in each case was solved by the numerical method [3].

The relative intensities were converted into absolute units by comparing the spectral intensities of the plasma and carbon arc (or tungsten lamp) and taking into account the geometry of the systems: radiation source — calibrating system — spectrogramme — microphotometer — density recording and exposure times.

Temperature determination

The plasma temperature was measured by the "one spectral line" method. This method employs the relationship between temperature and the intensity of a spectral line emitted by excited atoms (equation 1). For temperature measurements in gA determination, the argon Ar I lines 3554.31; 3567.66; 3606.52 Å were used for the Si I line, assuming the values of A_{nm} as given in [4]. For determination of relative transition probabilities of the Si II line, the temperature determined from the Ar I lines 4300.10; 4333.56 and 4266.29 Å was employed. The values of A_{nm} for these lines were taken from the same reference [4] which agree with the values given in [5] and [6].

The plasma temperature was found to oscillate between 5500 and 8200°K, depending on the place and section. The temperature found is roughly equal to the actual temperature of the plasma stream, since the addition of $SiCl_4$ into the argon plasma reduces the metastable Ar I states into the equilibrium condition which make it possible to avoid a serious error in temperature measurements by the "single spectral line" method in pure plasma generated by a noble gas [7].

Calculation of relative transition probabilities

After converting the values $I(x)$ into $I(r)$, the latter were substituted into equation (2) and the relative transition probabilities were calculated. The authors presented the results of their studies in a common form, giving the relative values of $g_n A_{nm}$.

By employing the method of converting (Ix) into (Ir) given in [3], an incorrect determination of $I(x)$ at one point (resulting from uneven distribution of emulsion, local disturbances in the plasma, etc.) affects not only the corresponding value of $I(r)$ but also the cloasest neighbouring values. This increases the scattering of results, and hence, the determination error.

On account of this, certain simplifications were made for the spectral lines whose excited level energies are equal or only slightly different.

The values $I(x)$ and $I(r)$ may be interrelated by the following equation:

$$I_i(x) = \sum_{j}^{j=i} B_{ij} I_j(r) \tag{4}$$

Taking into account equation (1), we obtain

$$I_i(x) = \sum_{j}^{j=i} \frac{1}{4\pi} N_j \frac{g_n}{Q(T_j)} \exp\left(-\frac{E_n}{kT_j}\right) A_{nm} h\nu_{nm} B_{ij}. \tag{5}$$

Considering the two spectral lines, one obtains

$$\frac{I_i^{(1)}(x)}{I_i^{(2)}(x)} = \frac{g_n^{(1)} A_{nm}^{(1)} \nu_{nm}^{(1)}}{g_n^{(2)} A_{nm}^{(2)} \nu_{nm}^{(2)}} \frac{\sum\limits_{j}^{j=i} Q(T_j)^{-1} N_j B_{ij} \exp\left(-\dfrac{E_n^{(1)}}{kT_j}\right)}{\sum\limits_{j}^{j=i} Q(T_j)^{-1} N_j B_{ij} \exp\left(-\dfrac{E_n^{(2)}}{kT_j}\right)}. \tag{6}$$

If the excited level energies of two spectral lines are equal, $E_n^{(1)} = E_n^{(2)}$ the ratio of their $g_n A_{nm}$ values will be given by the equation

$$\frac{g_n^{(1)} A_{nm}^{(1)}}{g_n^{(2)} A_{nm}^{(2)}} = \frac{I_i^{(1)}(x)\,\nu^{(2)}}{I_i^{(2)}(x)\,\nu^{(1)}} \tag{7}$$

When the excited level energies of two given lines are only slightly different, we can assume a certain temperature range that the value of "b" is

$$b = \exp - \frac{E_n^{(2)} - E_n^{(j)}}{kT} \tag{8}$$

and is approximately constant. The lesser the energy difference $E_n^{(2)} - E_n^{(1)}$ and the relative temperature change over a given temperature range are the smaller is the error committed, assuming $b = $ const.

$\Delta E = -0.02$ eV $T\,[°\text{K}]$	8500	8000	7500	7000	6500	6000	5500
$\exp\left(-\dfrac{\Delta E}{kT}\right)$	1.03	1.03	1.03	1.03	1.04	1.04	1.04
$\Delta E = -0.18$ eV $T\,[°\text{K}]$	8500	8000	7500	7000	6500	6000	5500
$\exp\left(-\dfrac{\Delta E}{kT}\right)$	1.28	1.30	1.32	1.34	1.38	1.42	1.48

Taking into account equation (8), expression (6) on transformation will assume the form

$$\frac{g_n^{(1)} A_{nm}^{(1)}}{g_n^{(2)} A_{nm}^{(2)}} = \frac{I_i^{(1)}(x)\,\nu^{(2)}}{I_i^{(2)}(x)\,\nu^{(1)}} \cdot b. \tag{9}$$

In order to increase the accuracy of calculations, the $I(x)$ plot for a given line was divided into parts and the mean value of b was used in a given temperature range. The use of the above method of calculation simplified the laboirous computations somewhat and helped to decrease the scattering of the results.

Results

The results of our work and those of other authors given in Table I on transition probabilities of the Si I lines, do not exhaust all papers on that subject.
The values of oscillator strengths or transition probabilities for some of the lines in Table I were also determined by Savage [14] and Addink [15].

TABLE

Å [Å]	E_m [eV]	E_n	$J-J$	gA — experimental				gA — theoretical		
				this work	[8]·10⁷ absolute	[9] relative	[10]·10⁷ absolute	[11] relative	[12]·10⁷ absolute	[13]·10⁷ absolute
2207.98	0.00	5.61	0—1	10.9	3.0		5.67			5.32
2210.89	0.01	5.62	1—2	16.5	3.0		13.6			12.1
2211.74	0.01	5.61	1—1	8.10			4.25			4.27
2216.67	0.03	5.62	2—3	17.9	5.3		25.2			23.3
2218.06	0.03	5.62	2—2	9.55			4.1			4.60
2218.91	0.03	5.61	2—1	0.827						84.7
2278.28	1.91	7.35	0—1	2.07						0.109
2289.61	1.91	7.32	0—1	0.640						4.30
2291.03	0.78	6.19	2—3	1.07						0.229
2295.40	0.78	6.18	2—2	4.27						0.290
2303.06	1.91	7.29	0—1	26.1						23.0
2438.77	0.00	5.08	0—1	1.36				0.25	0.224	0.138
2443.36	0.01	5.08	1—1	1.18				0.229	0.210	0.158
2452.12	0.03	5.08	2—1	1.00				0.168	0.182	0.111
2506.90	0.01	4.95	1—2	79.7	63	31.4	20.5	32	20.9	22.1
2514.32	0.00	4.93	0—1	71.2	57	25.6	16.5	25.3	37.2	17.4
2516.11	0.03	4.95	2—2	127	130	91	62.0	95.5	27.3	65.3
2519.20	0.01	4.93	1—1	69.3	43	19.3	12.0	18.7	12.2	12.9
2524.11	0.01	4.92	1—0	73.4	84	25.9	15.4	25.3	16.3	17.3
2528.51	0.03	4.93	2—1	80.3	71	31	21.0	31.3	20.2	21.4
2532.38	1.91	6.80	0—1	24.8						2.13
2568.64	1.91	6.73	0—1	3.85						0.115
2577.15	1.91	6.72	0—1	0.941						0.124
2881.58	0.78	5.08	2—1	277	150	78		83.5	54.3	66.3
2970.35	0.78	4.95	2—2	0.146				0.019	0.0112	0.0114
2987.65	0.78	4.93	2—1	5.87	6.3			0.701	0.666	0.566

Table II shows the relative values of gA several Si II lines and the results of other authors concerning the same lines. The values of gf for the analyzed Si II multiplets are given in papers [21–24], apart from papers cited by the authors. The values of $g_n A_{nm}$ taken

TABLE II

λ [Å]	E_m [eV]	E_n	$J-J$	g_A — relative					
				this work	[16]	[17]	[18]	[19]	[20]
3853.66	6.83	10.03	$\frac{3}{2}-\frac{3}{2}$	0.117	0.105	0.182	0.108	0.111	0.114
3856.02	6.83	10.03	$\frac{5}{2}-\frac{3}{2}$	1.00	1.00	1.00	1.00	1.00	1.00
3862.59	6.83	10.02	$\frac{3}{2}-\frac{1}{2}$	0.550	0.325	0.573	0.573	0.551	0.555
4128.05	9.79	12.78	$\frac{3}{2}-\frac{5}{2}$	4.96	4.50	5.77	7.79	15.4	0.785
4130.88	9.80	12.78	$\frac{5}{2}-\frac{7}{2}$		7.14				
4130.88	9.80	12.78	$\frac{5}{2}-\frac{7}{2}$	7.51	0.357	6.93	11.8	23.0	1.18

from other papers are given in Table I, preserving the type of scale used by each particular author. Table II has a unified scale, assuming the value of $g_n A_{nm}$ for the line 3856.02 Å as a reference point.

The data concerning the wavelengths, energies, transitions and quantum number J were assumed according to [25].

Determination error

The error committed when determining the relative transition probabilities consists of the errors committed in the determination of spectral line intensities and the value of the expression $\exp\left(-\dfrac{E}{kT}\right)$. The error of intensity determinations occurs during photometering of the line with a mictrophotometer, plotting of the density curve and photometering of the tungsten lamp or carbon arc spectrum.

The analysis has shown that the error committed in determination of the $g_n A_{nm}$ values for the Si I lines does not exceed, in general, 20%, and for weak lines, 30%. In the case of the Si II lines the determination error does not exceed 12%.

REFERENCES

[1] A. Czernichowski, W. Żyrnicki, W. Mleczko, *Comptes Rendus*, **270**, ser. B 393 (1970).
[2] A. T. Hattengurg, *Appl. Optics*, **6**, 95 (1967).
[3] W. J. Pearce, *Conference on Extremely High Temperature*, Boston–Massachusetts ed. Fisher and Mansur, New York, John Willey and Sons 1958.
[4] B. S. Malone, W. H. Corcoran, *J. Quant. Spectrosc. Radiative Transfer* (GB), **6**, 443 (1966).
[5] P. B. Coates, A. G. Gaydon, *Proc. Roy. Soc. (London), Ser. A*, **293**, 452 (1966).
[6] B. D. Addock, W. E. G. Plumtree, *J. Quant. Spectrosc. Radiative Transfer.*, (GB), **4**, 29 (1964).
[7] A. Czernichowski, J. Chappelle, F. Cabannes, *Comptes Rendus*, **270**, ser. B, 51 (1970).
[8] C. H. Corliss, W. R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, NBS Monograph 53 (1962).
[9] I. J. Slavenas, *Optika i Spektrosk.*, **16**, 390 (1964).
[10] W. Hofmann, *Z. Naturforsch.*, **24a**, 990 (1969).
[11] M. Z. Kokhlov, *Izv. Crim. Astrofiz., Obser.* **26**, 52 (1961).
[12] G. M. Lawrence, *Astrophys., J.*, **148**, 261 (1967).
[13] B. Warner, *Mon. Not. R. Astr. Soc.*, **139**, 1 (1968).
[14] B. D. Savage, G. M. Lawrence, *Astrophys. J.*, **146**, 940 (1966).

[15] N. W. Addink, *Spectrochim. Acta*, **14**, 349 (1959).

[16] E. Shulz-Gilde, *J. Quant. Spectrosc. Radiative Transfer.*, **9**, 13 (1969).

[17] B. Woodgate, *Mon. Not. R. Astr. Soc.*, **134**, 287 (1966).

[18] Ch. Froese, A. B. Underhill, *Astrophys. J.*, **146**, 301 (1966).

[19] H. G. Groth, *Z. Astrophys.*, **51**, 231 (1960).

[20] R. H. Garstang, L. J. Shamey. *Proc. NASA-AAS Symp. on Magnetic and Other Peculiar A Stars*, Nov. 1965 (1967).

[21] P. Hey, *Z. Phys.*, **157**, 79 (1959).

[22] H. R. Griem, *Plasma spectroscopy*, New York, McGraw-Hill 1964.

[23] Ch. Froese Fisher, *Astrophys. J.*, **151**, 759 (1968).

[24] L. Biermann, K. Lubeck, *Z. Astrophys..*, **25**, 325 (1948).

[25] A. R. Striganov, N. S. Sventitskii, *Tablitsy spektralnykh linii neitralnykh i ionizovannykh atomov*, Moskva 1966.