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# Bonding in Mg<sub>2</sub>Si Studied with X-ray Photoelectron Spectroscopy

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We have prepared samples of Mg<sub>2</sub>Si on atomically clean Si(100) surfaces under ultrahigh vacuum conditions and used X-ray photoelectron spectroscopy to study the nature of the chemical bond. Values for the charge transfer between Si and Mg are derived from the XPS spectra and compared with values determined theoretically. An ionicity of 9% was predicted from the theory, which agrees well with the value of 8% derived from the size of the chemical shift associated with the XPS spectra.

## Introduction

The bonding in magnesium silicide has been the subject of many studies in the past.<sup>1–5,16</sup> One of the questions remaining is the degree of ionicity in the Mg–Si bond; the reported values differ by as much as 90%, i.e. from a nearly ionic compound to one that is almost totally covalent with 10% ionicity.<sup>1–5</sup> In all these studies the Mg<sub>2</sub>Si had been exposed to air. Mg<sub>2</sub>Si is highly reactive with the water vapor in air, so extensive exposure will result in a sample that has at least an outside layer of MgO and SiO<sub>2</sub>, corrupting all surface sensitive techniques.

The determination of bonding in solids with X-ray photoelectron spectroscopy (XPS) is a well established technique.<sup>6</sup> The exact value of the core level binding energy depends on the chemical state of the electron. The energies in the compound are thus shifted with respect to the binding energies in the pure elements. The change in valence charge density can be deduced from these shifts, giving an estimate of the ionicity of the bond.

In this paper we present an *in situ* XPS study of the ultrahigh vacuum (UHV) preparation of a magnesium silicide and show that the compound has a stoichiometric ratio of Mg:Si = 2:1, i.e. Mg<sub>2</sub>Si. This is the only stable magnesium silicide.<sup>7</sup> We have calculated the ionicity of the bond from the chemical shifts observed in the XPS experiments, using the potential model described below, and compared these with the results from the electronegativity model of Pauling.

## Theory

**1. Potential Model.** The chemical shift of a core level in an XPS experiment is induced by a change in the valence shell potential, Madelung potential, and relaxation energy. The valence shell potential is the interaction between the core and the valence electrons on the same atom. When an atom is involved in a chemical reaction, its valence electrons are rearranged and the valence shell potential is changed. In the reaction the atom will go from state A to state B (A → B); the change in its potential is given by<sup>8</sup>

$$\Delta E_c(A \rightarrow B) = K_c [q_v^A - q_v^B] \quad (1)$$

where  $q_v$  is the charge of the valence shell and  $K_c$  is the coupling between the core and the valence electrons. If the valence charge is considered to be a screening charge, the coupling constant is

$$K_c = \frac{e^2}{r_v} \quad (2)$$

where  $r_v$  is the average radius of the valence shell in Bohr units and  $e$  is the electron unit charge. The effect of this potential on a core electron is diminished by the Madelung potential, which is the potential between the core electron and all other charges present in the solid. If these charges are considered to be point charges ( $q_j$ ), the Madelung potential becomes

$$V_i = \sum_{j \neq i} \frac{q_j}{R_{ij}} \quad (3)$$

where  $R_{ij}$  is the distance between the core electron  $i$  and charge  $j$ ; this is the interatomic distance if we consider the core electron to be placed at the nucleus. The value of this potential has the opposite sign of the first term.

There may also be a change in the relaxation energy ( $E_c^R$ ), which can be split into two contributions, intra- and extraatomic. The equation for the chemical shift then can be written as

$$\Delta E_c(A \rightarrow B) = \frac{e^2}{r_v} [q_v^A - q_v^B] + [V_i^A - V_i^B] + E_c^R \quad (4)$$

If we make the following assumptions, (i) the radius of the valence shell does not change, (ii) we sum in the Madelung potential only over the nearest neighbors, and (iii) we replace  $q_j$  with  $\Delta q_v$  as the charge is transferred to the neighboring atom, then we can rewrite (4) into the following form

$$\Delta E_c = \Delta q_v e^2 \left( \frac{1}{r_v} + \frac{n}{R} \right) + E_c^R \quad (5)$$

where  $n$  is the number of nearest neighbors and  $R$  is the intraatomic distance in Bohr units.

**2. Pauling's Electronegativity Model.** From the electronegativity values of two atoms, the ionicity of a bond formed between them can be estimated.<sup>9</sup> Pauling found a relation between the ionicity of a bond and the difference in electronegativities of the atoms forming the bond<sup>10</sup>

$$I = 1 - \exp[-0.25(\chi_a - \chi_b)^2] \quad (6)$$

where  $I$  is the ionicity, which is the fractional amount of ionic charge, and  $\chi_a$  and  $\chi_b$  are the electronegativities of atoms  $a$  and  $b$ . The charge transfer is then given by

<sup>Ⓞ</sup> Abstract published in *Advance ACS Abstracts*, April 15, 1995.

$$q = n \left[ \frac{\chi_a - \chi_b}{|\chi_a - \chi_b|} \right] I \quad (7)$$

where  $n$  is the number of bonds per atom. Application of this model to  $\text{Mg}_2\text{Si}$ , with electronegativities of 1.8 for silicon and 1.2 for magnesium, results in a charge transfer of 0.18 charge units per bond. This indicates an ionicity of 9%, since magnesium is divalent.

### Experimental Section

Magnesium silicide was grown on a Si(100) substrate, which was cut from a commercial n-type wafer. It was chemically treated before it was brought into the UHV chamber. The chemical treatment used is described elsewhere<sup>11</sup> and resulted in the growth of a thin protective oxide layer. Under UHV conditions the Si substrate could be heated by passing a current directly through it. The substrate was outgassed at 500 °C for approximately 12 h before the chemically grown oxide layer was removed. The removal of the oxide layer was done by heating the sample up to 900 °C for 5 min. The magnesium was evaporated from a Knudsen cell, held at temperatures between 300 and 370 °C, onto the silicon substrate, which was kept at room temperature. The deposition rate was monitored using a quartz crystal microbalance. During the deposition the pressure did not exceed  $1 \times 10^{-9}$  mbar. After depositing between 500 and 1000 Å, the substrate was heated up to 180 °C for 20 min. Silicide formation and contamination levels (O 1s and C 1s core levels) were monitored with XPS. Contaminants were routinely below the detection limit of the apparatus, indicating a level of less than a few percent. Unmonochromated Mg K $\alpha$  X-rays were used in all measurements. The detector has a hemispherical analyzer, fitted with two microchannel plates followed by a strip with 16 gold anodes as the electron detector.

Analysis of the XPS data was performed using a least squares routine that synthesizes a fit composed of Voight functions after the removal of an appropriate Shirley-type background. In the Mg 1s core level data, of the pure metal spectra presented, there is an asymmetry. A Doniac Šušnić-type parameter<sup>8</sup> had to be included in the fit parameter set in order to describe this asymmetry. This feature is only observed in metals and can be used to identify a solid as a metal.<sup>11,12</sup>

### Results and Discussion

After the preparation of the sample the stoichiometric ratio of the compound was determined by comparing the areas under the Mg and Si core level spectra (Table 1). The peak intensities in the spectra can be described by the following equation for the intensity  $I$  (c/s)

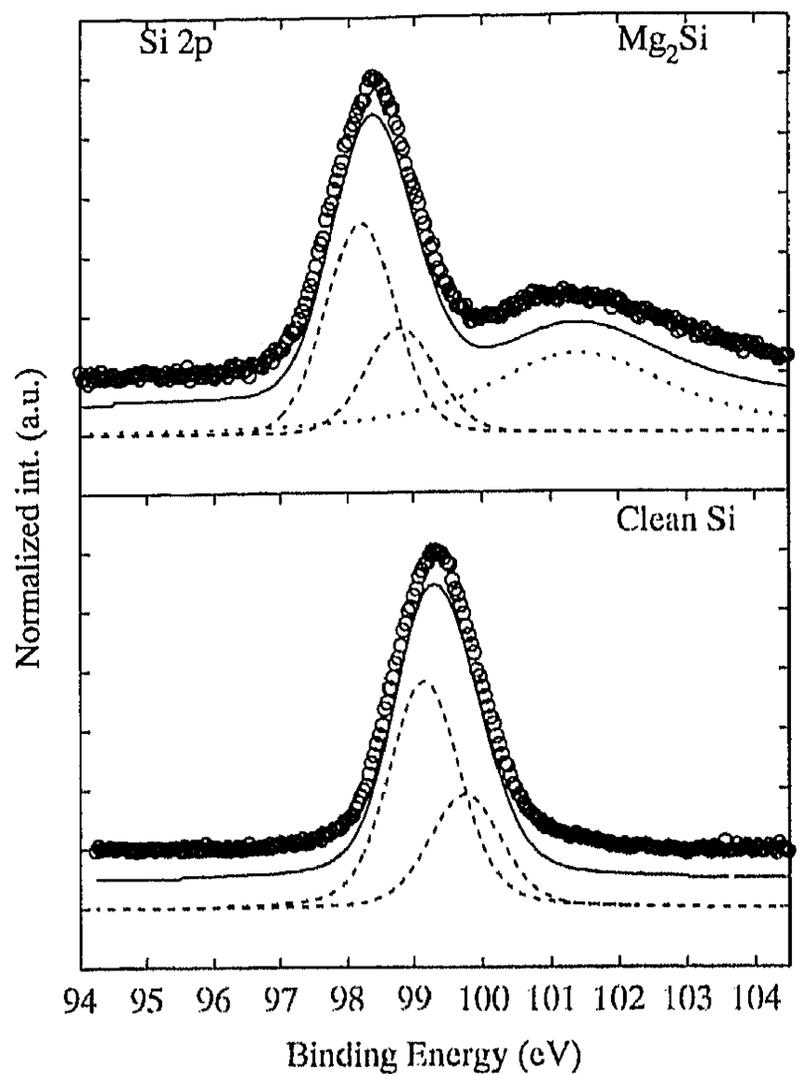
$$I = N\sigma\lambda t \quad (8)$$

where  $N$  is the number of atoms involved,  $\sigma$  is the cross section,  $t$  is the transmission function of the analyzer, and  $\lambda$  is the electron mean free path. The transmission function can be described by

$$t \propto (\sqrt{E_{\text{kin}}})^{-1} \quad (9)$$

where  $E_{\text{kin}}$  is the kinetic energy of the detected electron for kinetic energies between 2 and 200 times the pass energy of the analyzer. The mean free path of an electron has been described by Seah and Dench<sup>13</sup> and has the following proportionality for electrons with kinetic energies higher than 150 eV

$$\lambda \propto \sqrt{E_{\text{kin}}} \quad (10)$$



**Figure 1.** Si 2p core level spectra for the clean silicon (bottom panel) and silicide (top panel). The raw data and fit curve have been shifted upward for clarity. Open circles represent the raw data after background subtraction. The solid line is the fit curve, the dashed lines are the fit components, and the dotted line is the plasmon; see text for details.

**TABLE 1: Areas ( $A$ ) and Effective Areas ( $A/\sigma$ ) under the Core Peaks of  $\text{Mg}_2\text{Si}$**

	$A$ (ceV/s)	$A/\sigma$ (ceV/s m <sup>2</sup> )
Mg 2p	0.28	36.6
Mg 2s	0.51	46.0
Si 2p	0.36	18.9
Si 2s	0.33	18.1

The transmission function and the electron mean free path now cancel, so the number of atoms contributing to the peak can now be estimated by the ratio of the area over the cross section. In Table 1 the area ( $A$ ) and the effective area ( $A/\sigma$ ) are presented; note the difference between the Mg 2s and Mg 2p areas. This difference is caused by the Si 2p satellite intensity derived from the Mg K $\alpha_{3,4}$  radiation. These electrons have the same kinetic energy as the electrons of the Mg 2s core level from the Mg K $\alpha_{1,2}$  radiation. Consequently only the Mg 2p peak was used to determine the ratio between Si and Mg. The stoichiometry was calculated as Mg:Si = 2:1, and the compound is thus identified as  $\text{Mg}_2\text{Si}$ , in agreement with other results which state that this is the only known stable stoichiometry for a magnesium silicide.<sup>7,14</sup>

In Figures 1–4 the magnesium and silicon core level spectra from the constituent elements and the silicide are presented. The open circles are the raw data, the solid line is the fit, and the dashed lines represent the components. In the p level spectra the spin orbit contributions are plotted separately. From the top panels of Figures 1–4 (silicide) it can be seen that there are no extra components present, indicating that there is no unreacted Mg or Si. The pure Mg spectra have a clear asymmetric or Doniac Šušnić line shape, which is characteristic of a metal and is caused by shake-up processes. The asymmetry is not present in the Mg spectra derived from the silicide, indicating a transition from a metallic to a nonmetallic compound. This is in agreement with other studies<sup>15</sup> which state that  $\text{Mg}_2\text{Si}$  is a small-gap semiconductor with an indirect band

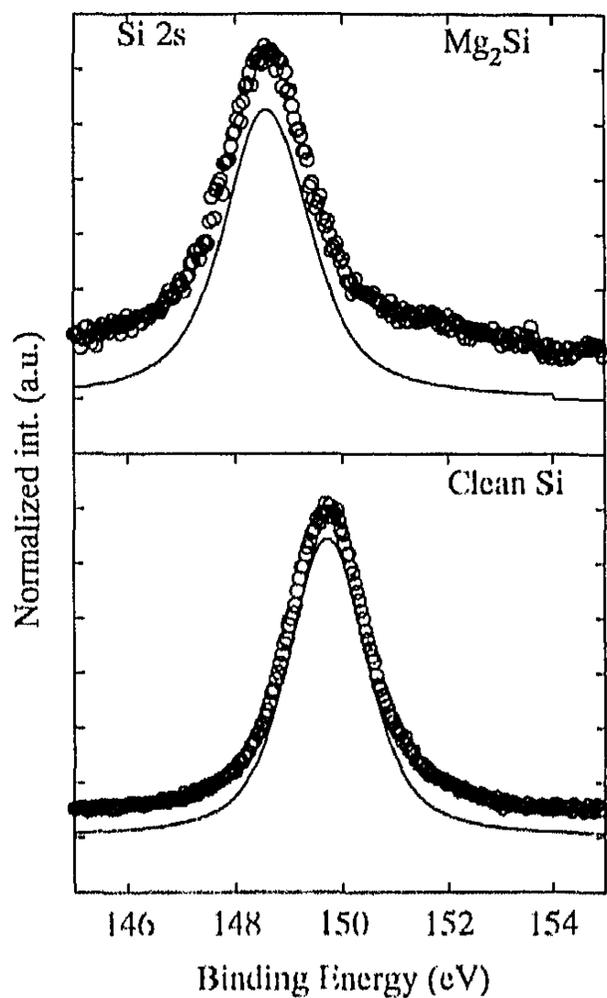


Figure 2. Si 2s core level spectra for the clean silicon (bottom panel) and silicide (top panel). The legend is the same as that for Figure 1.

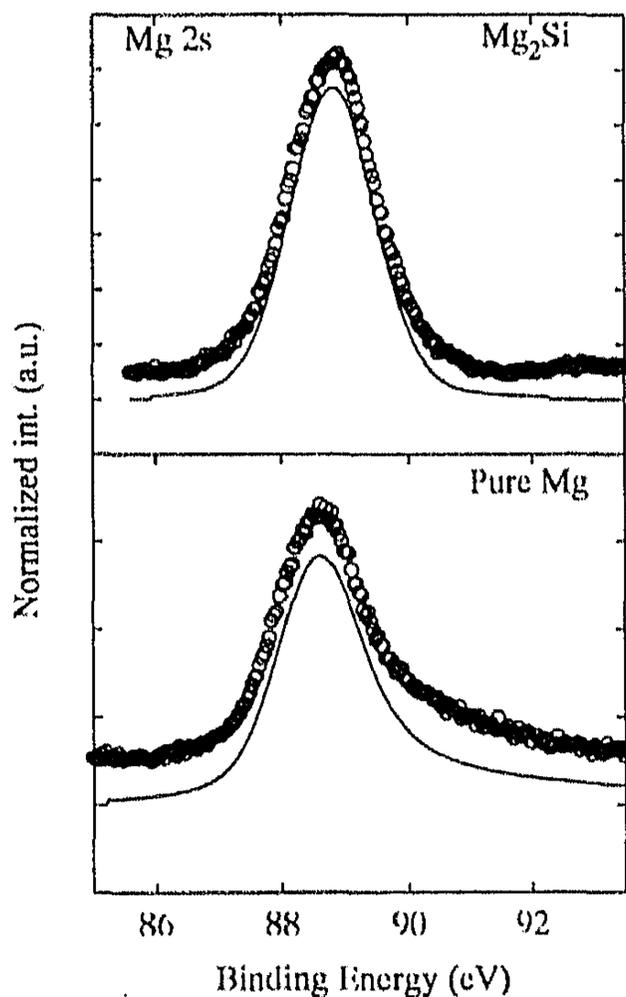


Figure 3. Mg 2p core level spectra for the pure magnesium (bottom panel) and silicide (top panel). The legend is the same as that for Figure 1.

gap of 0.7 eV. The peak at 101.2 eV in the Si 2p spectrum can be attributed to a plasmon loss associated with the Mg 1s electrons. The plasmon energy can be estimated from the Drude model

$$E_p = \hbar \sqrt{\frac{4\pi n e^2}{m}} \quad (11)$$

where  $m$  is the electron mass,  $e$  is its unit charge, and  $n$  is the average electron density in the unit cell. Assuming that only the valence electrons contribute to the plasmon, we use 32 for the number of electrons and 6.48 Å for the lattice constant. This

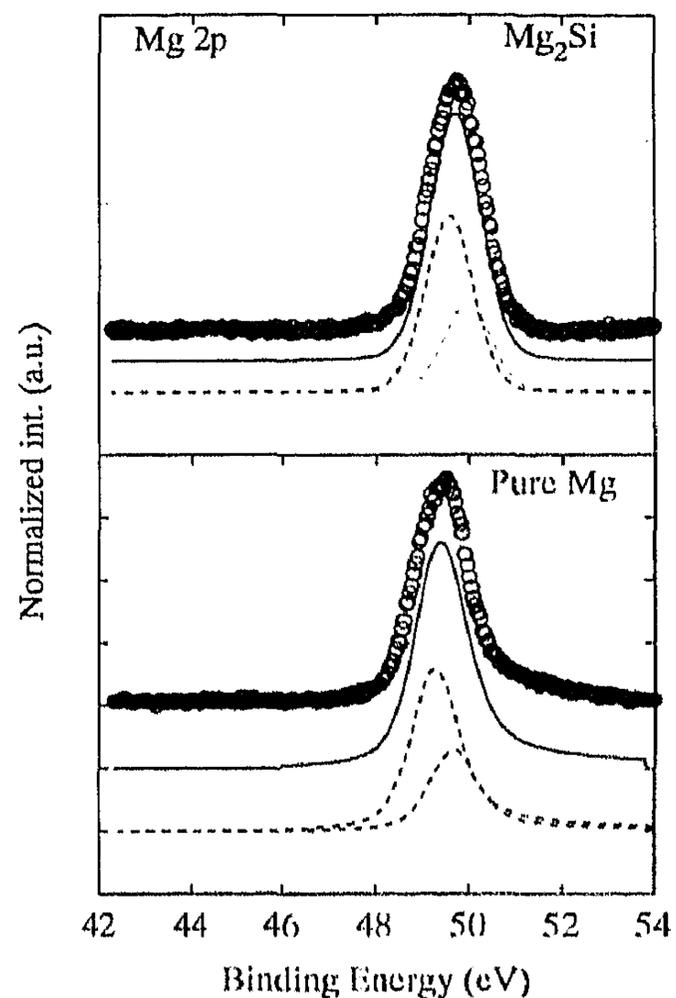


Figure 4. Mg 2s core level spectra for the pure magnesium (bottom panel) and silicide (top panel). The legend is the same as that for Figure 1.

TABLE 2: Energy Shifts (eV) of the Magnesium and Silicon Peaks in Magnesium Silicide with Respect to the Pure Compounds

	Mg shift (eV)	Si shift (eV)
2p	0.3	0.95
2s	0.2	1.1
mean shift	0.25	1.02

gives a plasmon energy of 13 eV, which is in good agreement with the experimental value of 12.4 eV.

The energy shifts of the Si and Mg core levels in Mg<sub>2</sub>Si with respect to those from the pure elements are presented in Table 2. The Mg core levels shift in the opposite direction with respect to the Si core levels. The mean shifts are +0.25 eV for the Mg core levels and -1.02 eV for the Si core levels. These shifts are in good agreement with the shifts reported by Wigren *et al.*,<sup>14</sup> who found +0.34 and -0.9 for the Mg and Si levels, respectively. They performed photoemission measurements on the initial interface formation of Mg on Si(111) at room temperature. The formation of Mg<sub>2</sub>Si at the Mg/Si interface was also reported by van Buuren *et al.*<sup>11</sup> for Mg on Si(100). Ghosh *et al.*<sup>16</sup> also performed XPS experiments on Mg<sub>2</sub>Si. They found a shift of 0.7 eV for both Mg and Si core levels; however, their samples were prepared *ex situ*. We have attempted to repeat their preparation conditions, but the samples invariably have too high an oxygen content. Furthermore, the ratio between Si and Mg did not indicate that we were measuring magnesium silicide. They also report the presence of oxygen in their samples but consider that this will not influence the Mg core levels in magnesium silicide excessively. However their Si 2p peak is much too small, indicating that the silicide is either buried under a thick MgO layer or the stoichiometry is not Mg:Si = 2:1.

From the shift presented in Table 2 the amount of charge transfer can be calculated using the potential model. The relaxation term in eq 6 can be split into two contributions, as described in the Theory section. The intraatomic contribution refers to the rearrangements of the electrons on the atom itself; these are assumed to be nearly unaffected by the changes in

**TABLE 3: Net Charge Transfer Values per Bond Calculated with the Potential Model  $r_v$  Valence Shell Radius from Carlson<sup>9</sup> and  $R$ , the Interatomic Distance**

	$r_v$ (in Bohr units)	$R$ (in Bohr units)	charge transfer
magnesium	2.31	5.23	0.18
silicon	1.97	5.23	0.15

the chemical environment.<sup>7</sup> The extraatomic contribution is more complicated to estimate. In general this involves the charge flow from neighboring atoms. This is large in highly polarizable systems. From the small difference in electronegativity we can deduce that the bond in Mg<sub>2</sub>Si is covalent and that the extraatomic relaxation is small. We therefore assume the  $E_c^R$  contribution to be negligible. The results of these calculations plus the parameters used are listed in Table 3. For the radii of the valence shell we used the values given by Carlson.<sup>9</sup> We find that the charge transfer is 0.16 charge units from the magnesium to the silicon. The bonding is then covalent with an 8% ionicity, because magnesium is divalent. This result is in good agreement with the result of Pauling's electronegativity model (see Theory section). Estimates of the ionicity are reported in several papers.<sup>1-5,16</sup> Our result is in good agreement with the result of Eldridge *et al.*<sup>2</sup> and those of Whitten *et al.*<sup>5</sup> The former performed elasticity measurements and compared these with atomic radii. The latter calculated the frequencies of lattice vibrations in Mg<sub>2</sub>Si. From the calculations they obtained an ionicity of 25%. Ageev and Guseva<sup>1</sup> performed X-ray reflectivity measurements and concluded that the ionicity of Mg<sub>2</sub>Si must be much higher than 10%. From infrared reflectivity measurement McWilliams<sup>3</sup> found that the ionicity was 90%, indicating that Mg<sub>2</sub>Si is an ionic-like compound. From the above it is clear that the bulk sensitive techniques are more in agreement with our oxygen-free result. The more surface sensitive techniques used on *ex situ* prepared Mg<sub>2</sub>Si samples tend to find ionic-like compounds. From this we may conclude that the oxidized layer on the surface of the sample strongly influences the results. Bulk-like techniques are less sensitive to any surface contamination. In our experiments, although surface sensitive, there was no oxygen detected. It is clear that the oxygen-free results represent the true nature of the chemical bond between Si and Mg in Mg<sub>2</sub>Si.

### Conclusions

The silicide formed after heating silicon covered with magnesium has the stoichiometric ratio of Mg:Si = 2:1 and is

thus Mg<sub>2</sub>Si. The core level binding energies in this silicide are shifted with respect to the pure elements by +0.25 and -1.02 for the magnesium and silicon levels, respectively; from these we find that Mg<sub>2</sub>Si is a covalent compound with an ionicity of only 8%. In our samples the oxygen contamination was negligible. We believe that our results and the results from bulk sensitive experiments represent the true nature of the chemical bond in magnesium silicide, because in both cases oxygen does not influence the results. In the more surface sensitive experiments the presence of oxygen has to be checked and accounted for.

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