RF Plasma Processing of Silica

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The processing of silica in an rf plasma was studied with a new experimental system, the process being carried out entirely in the vapor phase. SiO and Si were obtained by either thermal decomposition of SiO₂ or reduction by H₂. No other reducing material (which, like C, may become a contaminant) was used. The products were collected along the reactor length and analyzed afterward. Temperatures in the reaction zone were measured spectroscopically. The high reaction rates occurring in the gas phase did compensate for the low residence times. A diffusional model for the buildup of solid reaction products is discussed. Vapor phase plasma reduction of silica with hydrogen proved to be more effective than thermal decomposition and much more effective than heterogeneous processing. The efficiency evaluation was made on the laboratory-scale level.

KEY WORDS: rf plasma; silica; thermal decomposition and reduction; modeling and experiments.

1. INTRODUCTION

The introduction of plasma technology in the field of chemistry has been the subject of intensive studies over the past two decades. Specific plasma features (e.g., high temperatures, high mass and heat transfer coefficients, etc.) have initiated a large amount of research work in high-melting materials processing, some processes now being carried out on an industrial scale. However, the yield of plasma heterogeneous reactions is considered to be still limited by insufficient residence time and relatively poor penetration of solid particles within the plasma, this being due mainly to the high temperature and viscosity gradients prevailing in the reaction medium. Hence the interest in the considered process carried out in the vapor phase.

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Demand is increasing for the use of elemental silicon. However, the conventional carbothermic reduction of silica, presently the main source of Si and SiO, is a time- and energy-consuming process. Moreover, it does not provide very pure products, leaving impurities (carbides and carbon residual) which have to be removed by special techniques. Thus, any new methods for silicon synthesis are worth investigating. From this results the high interest in fast one-stage plasma processing of silicon compounds.

At elevated temperatures the main silica decomposition reaction taking place under a neutral atmosphere can be written\(^{(5,6)}\)

\[
\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(_{\text{g}}) + \frac{1}{2}\text{O}_2(\text{g}) \quad (1)
\]

together with a significant contribution from the reactions:

\[
\text{SiO}_2(\text{l}) = \text{SiO}_2(\text{g}) \quad (2)
\]

and

\[
\text{SiO}(_{\text{g}}) = \text{Si}(_{\text{g}}) + \frac{1}{2}\text{O}_2(\text{g}) \quad (3)
\]

Above 3200 K, the following reaction prevails:

\[
\text{SiO}_2(\text{g}) = \text{SiO}(_{\text{g}}) + \frac{1}{2}\text{O}_2(\text{g}) \quad (4)
\]

Below 2200 K, the disproportionation process,

\[
2\text{SiO}(_{\text{g}}) = \text{SiO}_2(\text{s}) + \text{Si}(\text{s}) \quad (5)
\]

may occur as well. The high thermal stability of gaseous SiO is linked with its high bond energy (373.9 kJ \cdot \text{mol}^{-1}). The possible disproportionation process [Eq. (5)] during SiO condensation can be limited by fast quench of gaseous reactants. One should note that the plasma gas is usually used in a large excess, so that its concentration remains constant during the course of the reaction.

Calculations of the heat transfer to silica particles in a hot gas\(^{(7,8)}\) confirmed that the vaporization is the controlling step in high-temperature SiO\(_2\) thermal decomposition. Coldwell's\(^{(9)}\) model of the Si–O–C system allowed the calculation of the product composition when SiO\(_2\) and carbon are reacted in a plasma. Below a threshold temperature equal to 2400 K, SiO and SiC are the major products, while at higher temperatures elemental silicon is expected to appear. With SiO and hydrocarbons (as starting materials), the threshold temperature was lowered to 1000 K, thus making the process more technically feasible.

Amouroux et al.\(^{(10)}\) determined the reducing properties of the C–H–O system at elevated temperatures regarding its applicability to the direct reduction of silica. High temperatures and low pressure favor SiO\(_2\) reduction