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A study of flame acceleration and the possibility of detonation with silane mixtures

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ABSTRACT

Mixtures of silane and nitrous oxide are one of a number of gaseous reactants used in the final stages of semiconductor device fabrication processes and whose explosion properties in confined volumes such as exhaust gas piping systems are not known. In the present paper we report the results of theoretical and experimental studies of the propensity for flame acceleration and potential deflagration to detonation transition (DDT) hazard for silane–nitrous oxide mixtures in a 50 mm diameter pipe; together with an investigation of the effectiveness of nitrogen dilution as an explosion mitigation method. Preliminary results for ethylene–oxygen nitrogen are also presented from commissioning tests in the same apparatus to illustrate the explosion development process in a much studied explosive mixture. The experimental DDT limits are compared with criteria proposed by earlier investigators, based on detonation cell width. As no cell width data was available for the silane mixtures the cell widths used were those predicted using high temperature chemical reaction data.

1. Introduction

Silane is used extensively in the semiconductor manufacturing industry as a primary feedstock during the generation of a final protective layer of silicon oxide using chemical vapour deposition (CVD) techniques. Within the industry it is recognized that silane is potentially hazardous because of its pyrophoric nature. However little attention has been given to other possible combustion hazards that might be associated with silane. This could be a significant omission given that silane and the required oxidant may be present in premixed states prior to, as well as within and downstream of, a CVD reactor vessel; possibly in near stoichiometric ratios. In this document the potential detonation hazard arising with silane–nitrous oxide is explored both theoretically and experimentally.

In addition results are presented for ethylene–oxygen diluted with nitrogen whose pipe explosion and detonation characteristics are already well known (Thomas, 2008; Thomas et al., 2010).

2. Documented hazards involving silane

The predominant hazards involving silane discussed in the existing literature arise because of the pyrophoric behaviour exhibited by silane; the well documented fact that it instantaneously ignites when released to the atmosphere. The fires or explosions that may occur if the release is within a confined volume have been extensively discussed by Tamanini et al. (1998). A more recent study of silane fires and explosions following releases from bulk storage units is due to Ngai et al. (2007). A more general and widely cited review of silane and its chlorides is due to Britton (1990). Chen (2002) has also presented a review of silane fire and explosion hazards, as have Fthenakis and Moskowitz (1990). Hirano (2004) documents silane explosion incidents in Japan, most of which are attributed to spontaneous ignition.

One potential silane hazard that does not appear to have been considered by previous researchers is that of detonation. This is somewhat surprising as silane can obviously support extremely energetic exothermic chemical reaction to the extent that it was considered by McLain et al. (1985) as a potential component of a rocket propellant. Also, using a new flammability index (RF) Kondo et al. (2002) listed silane with an index value intermediate to those derived for acetylene and hydrogen, both of which are widely recognized as being easily detonated when mixed in stoichiometric proportions with an oxidant. Only one detonation incident is referred to in the published semiconductor literature when Bolmen (1998), discussing compressed gases, notes briefly a detonation event after an oxidant was accidentally introduced into a cylinder of silane. Pearce (2001) in a wider ranging discussion on protecting semiconductor facilities also makes passing reference to the possibility of detonation with silane, again without any detailed

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discussion of the relevant conditions. The only other reference to detonation in a silicon-based compound is by Miles et al. (1966) who considered the effect of silicon oxide condensation on the detonation properties of tetramethyl silane, which they found to be readily detonable when mixed with oxygen.

3. Flame acceleration and transition to detonation

3.1. Basic mechanisms

The basic mechanisms of flame acceleration and transition to detonation in process pipelines were reviewed recently by Thomas (2008).

Explosion events in pipelines, initiated by low energy sources ($E < 1$ J), first propagate as slow deflagrations. During this stage gas flow displacements ahead of the exothermic flame or reaction front are relatively small, the flame velocity relative to the pipe is also low ($<300\,m\,s^{-1}$) so that the pressure increase ahead of the flame is less that one bar and no shock wave is formed. As the flame front velocity increases, due to turbulent burning (deflagration) the overall explosion process may accelerate further. This is because of the positive feedback that arises following viscous interactions between unburnt gas ahead of the flame and the confining pipe walls. The resulting flow induced turbulence and consequential increase in the turbulent mass burning rate in the trailing deflagration front complete the feedback loop feeding energy released due to combustion as acoustic energy into the flow field ahead further increasing turbulence production ahead of the deflagration front.

It is often cited, but not fully quantified, that further escalation of the explosion process can occur as the velocity of the shock-flame complex approaches ca. $1000\,m\,s^{-1}$. Localised explosions now develop, with significant transient overpressures in some cases. This is termed deflagration to detonation transition (or DDT). Immediately following this macroscopic (Thomas, 2012) transition process the detonation wave moves faster than that predicted from simple steady state theory but is always decelerating and eventually reaches the steady or Chapman-Jouguet state. A true detonation will continue to propagate unsupported until the detonable mixture is exhausted or it is arrested or quenched by some appropriate mechanism or safety device.

3.2. Predicting detonation limits

Although thermodynamic calculations provide very accurate predictions of the properties of a detonation wave (pressure, velocity etc.) such calculations cannot predict whether a given detonation will or indeed can propagate under certain physical conditions. One reason for this is that a detonation wave is not a one-dimensional wave but, see Lee (2008) and Nettleton (1987), actually comprises a complex three-dimensional structure. Put simply, if this transverse structure can be generated or maintained within physical boundaries then detonation can be sustained.

This three dimensional structure is manifested as diamond like ‘cells’, imprints left on a lightly sooted surface, The characteristic sizes of the cells are related to the chemical reactivity of the system and these increase in size as the reactivity decreases. Test results from Dupre et al. (1985) in a range of pipe diameters suggest that detonation cannot propagate along a circular pipe when the ‘cell’ width is greater than a small multiple of D, where D is the diameter of the pipe. Also, the cell length, Λ, can be equated very crudely to some 100 times the induction or autoignition zone length of the von Neumann or induction zone. This zone length, L_i, is linked to the duration of the commencement and completion of the interlinked exothermal autoignition reactions. As the cell width, λ, is usually taken as 0.6 of the cell length Λ it might be possible therefore to estimate order of magnitude limits for the potential for detonation development using theoretical induction zone lengths computed from chemical kinetic reaction schemes or alternatively, from existing or new dedicated cell size measurements.

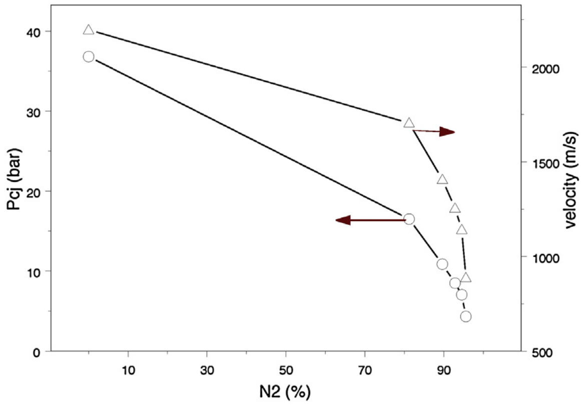

Fig. 1. Variation in calculated CJ detonation pressures and velocities as a function of nitrogen dilution; mixture $SiH_4 + 3.64N_2O + X\%N_2$;initial temperature – 293 K.

4. Present theoretical predictions

The section introduces the theoretical calculation methods used to estimate the detonation properties of silane–nitrous oxide mixtures diluted with nitrogen. Wherever possible attempts have been made to identify suitable pre-existing data against which each technique or specific calculation input could be validated. The specific calculations attempted were: Theoretical calculation of Chapman Jouguet (CJ) values of pressure and velocity; Estimates of characteristic detonation cell widths, λ, based on chemical kinetic reaction rate calculations.

4.1. Chapman-Jouguet properties

CJ detonation pressures and velocities were calculated using the GASEQ chemical equilibrium calculation software (GASEQ). This is a general purpose chemical equilibrium calculation program that seeks composition solutions by minimizing the Gibbs free energy of the possible reaction product species as a function of temperature and pressure. For detonation calculations there is an additional constraint arising from the requirements of the gas dynamic nature of the theoretical CJ solution. To obtain a solution the user is required to supply the appropriate thermodynamic data for all species available for use in the calculation.

Chapman Jouguet detonation pressures and velocities calculated using the above for silane–nitrous oxide–nitrogen as a function of nitrogen dilution are presented in Fig. 1. These data would seem to suggest that an asymptotic limit exists for a nitrogen dilution of ca. 90%, at which the theoretical detonation pressures and velocity decrease significantly; although as will be shown later, this is of no practical relevance.

4.2. Detonation cell width predictions

Despite the success of simple one-dimensional theories in describing and predicting detonation properties it is found that in practice detonations exhibit a complex multi-dimensional structure. This structure has been widely studied, especially using the smoked-foil technique where diamond like ‘cell’ imprints left on a lightly sooted surface (Nettleton, 1987). The characteristic sizes of the cells are related to the chemical reactivity of the system and increase in size as the reactivity decreases or the initial pressure