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A Mössbauer study of Kr incorporations in sputtered a-Si films

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Abstract. Krypton atoms incorporated in sputtered a-silicon films are investigated by means of ^{83}Kr Mössbauer spectroscopy. The hyperfine parameters of the ^{83}RbI source were determined by taking a spectrum against solid krypton. Mössbauer spectra were taken for films containing krypton concentrations up to 7 at.%. A Debye temperature of 116(4) K has been measured for a sample containing 2.83 at.% Kr. The isomer shifts found for all spectra and the high Debye temperature indicate that krypton resides in small highly pressurized precipitates.

1. Introduction

Ar atoms are introduced into Si in various materials processing techniques like ion-assisted deposition, sputtering and ion milling. It is therefore of interest to study the incorporation process and the sites of noble-gas atoms in amorphous and crystalline Si. Recently Greuter *et al* [1, 2] reported on a detailed study of 0.5–6 at.% Kr in a-Si films grown by plasma sputter deposition, using high-resolution electron microscopy (HREM), x-ray microanalysis, Rutherford backscattering (RBS), positron beam analysis, Raman spectroscopy, Mössbauer spectroscopy and bending measurements. There is a clear indication that ion-assisted growth leads to a strong reduction of open volume and that krypton resides in small agglomerates. The strongest argument for the presence of very small clusters comes from the Mössbauer data, from which a lower limit of 250 K was derived for the effective Debye temperature of the Kr atoms. Atomistic simulations showed that such a high value is only compatible with Kr monomers and trimers in the Si network.

An unsatisfactory aspect of the Mössbauer measurements of Greuter *et al* [1] is the fact that the data did not show any temperature dependence of the recoilless fraction, only fluctuations due to a varying peak–background ratio. We therefore decided to repeat these measurements and to study also the Kr concentration dependence.

2. Experimental details

The High Dose Desorption Spectrometer at IRI Delft was used to grow the films. Electrons emitted by filaments are accelerated up to an energy of 50 eV and are kept on a helical

trajectory by an external magnetic field. These electrons ionize the krypton gas introduced at a pressure of 0.01 to 0.1 Pa. A negative potential of 1.5 kV was used to sputter silicon neutrals from the target, while a negative potential of 50 V was periodically applied to the substrate in order to direct krypton ions towards the continuously growing film. This potential difference between the plasma and the substrate accounts for both implantation of the krypton ions and sputtering of the film.

Growth rates of the order of $7 \mu\text{m h}^{-1}$ and fluxes of sputtered target atoms and inert-gas ions of about $10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ can be reached. The Kr–Si flux ratio was varied between 0.5 and 6. Various inert-gas concentrations in the growing film were achieved by pulsating the inert-gas ion flux with different duty cycles at 0.5 Hz.

In a HREM picture of a deposited sample a layered structure can be observed [1]. The difference in contrast is the effect of different krypton concentration in the sublayers while the period is the result of Kr injection with a certain duty cycle at a frequency of 0.5 Hz. This means that the local Kr concentration varies along the depth, while only the average concentration is known.

a-Si films containing 0.35, 2.83, 5.13 and 6.67 at.% Kr were deposited on Be substrates at a temperature of 310 °C. The average krypton concentration was determined using a JEOL JXA 733 electron probe microanalyser. The intensities of $K\alpha$ rays of Si and $L\alpha$ rays of Kr were measured and compared with intensities of pure Si and with a Si–Kr standard having a uniform Kr concentration of 5.8 at.%.

Be was used as a substrate because of its transparency to the 9.4 keV Mössbauer gamma rays of ^{83}Kr .

^{83}RbI was used as a Mössbauer source. In comparison with $^{83}\text{RbHF}_2$ and $^{83}\text{RbCl}$, ^{83}RbI shows a narrower line [3, 4]. Dehydration at 100 °C for half an hour under H_2 flow narrows the line even more and decreases the intensity of the additional quadrupole component.

The Mössbauer measurements were performed in transmission geometry. The spectra as a function of Kr concentration were taken at 4.2 K. Several measurements as a function of absorber temperature were performed on the sample containing 2.83 at.% Kr. Six temperature points ranging from 4.2 to 250 K were chosen for the absorber, while the source was kept at 4.2 K.

3. Results and discussion

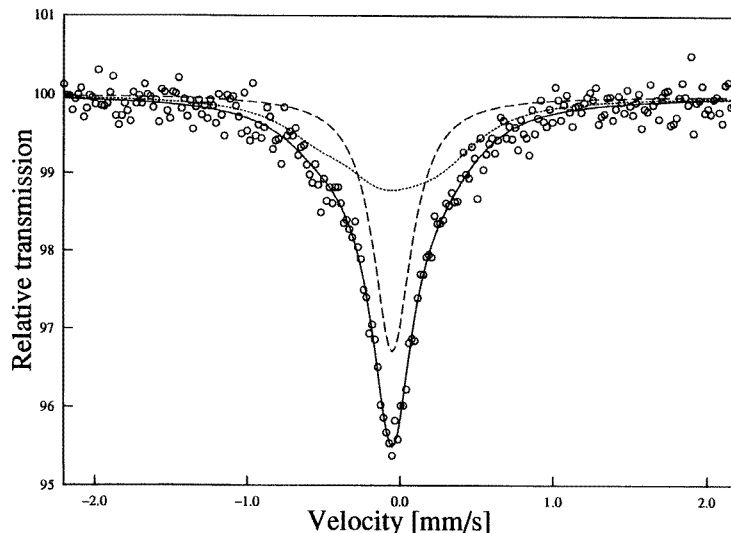
Greuter *et al* [1] have developed a model for the concentration of Kr incorporated in Si films grown by plasma sputter deposition as a function of Kr–Si flux ratio. According to this model, the Kr concentration increases from 0.3 to 2.5 at.% for Kr–Si flux ratios between 0.1 and 1. A maximum concentration of about 5.5 at.% is reached for a Kr–Si flux ratio of 5. A decrease in the concentration occurs upon further increase of the Kr–Si flux ratio because sputtering is playing a dominant role at high Kr fluxes.

The lower Kr concentrations of the samples prepared for the Mössbauer experiments are very well described by the ascendent part of the model curve of Greuter, while the highest concentration is appreciably larger than the predicted maximum even though it appears at the ‘right’ Kr–Si flux ratio.

The Mössbauer spectrum of the ^{83}RbI source versus solid Kr at 4.2 K consists of a single line and a quadrupole-split component, as can be seen in figure 1. Table 1 includes the relative areas of the quadrupole component A_q and of the single line A_s , the isomer shifts of both components S_q and S_s , the quadrupole coupling constant Δ_q and the linewidths Γ_q and Γ_s . These hyperfine parameters are in reasonable agreement with those given by Greuter and Niesen [3]. A comparison with their results shows that the present source was

Table 1. The hyperfine parameters of the source, all given in mm s^{-1} .

A_q/A_s	S_q	S_s	Δ_q	Γ_q	Γ_s
1.4(3)	-0.02(1)	-0.05(1)	0.9(2)	0.7(1)	0.29(2)

**Figure 1.** The Mössbauer spectrum of the ^{83}RbI source against solid Kr.

not completely dehydrated, probably because the source transfer from the glove box to the cryostat was not fast enough. Nevertheless the source spectrum is quite narrow compared to that of the KrSi samples.

Figure 2 shows the Mössbauer spectra of the various samples taken at 4.2 K. It is obvious that the shape of the spectra does not change much with increasing Kr concentration. All spectra were fitted assuming the presence of a single line and a quadrupole-split component. A special computer program which takes into account the fact that the source is not a single line [3] was used to fit the spectra. The program is based on an analytical deconvolution technique, taking the source parameters as input. It allows one to fit a series of spectra with the same values of hyperfine parameters and linewidths. The latter feature was used for spectra taken on the same sample at different temperatures.

The relative intensities of the single line and the quadrupole-split component are plotted in figure 3 as functions of the (average) Kr concentration. Because for this low-energy transition the recoilless fraction at 4.2 K is very close to 1 irrespective of the effective Debye temperature, the relative intensities can be considered as the relative fractions of Kr atoms in different environments. Increasing the Kr concentration will lead to an enhanced probability of clustering and to an increased size of the Kr clusters (precipitates). Therefore the concentration dependence suggests that the single-line component is associated with Kr atoms surrounded by other Kr atoms in a small precipitate the ('bulk' fraction), whereas the quadrupole-split component is associated with Kr atoms at the interface of a precipitate. This is analogous to the interpretation of Mössbauer spectra of ^{83}Kr precipitates in Al [3]. The observed concentration dependence rules out an interpretation of the single line as

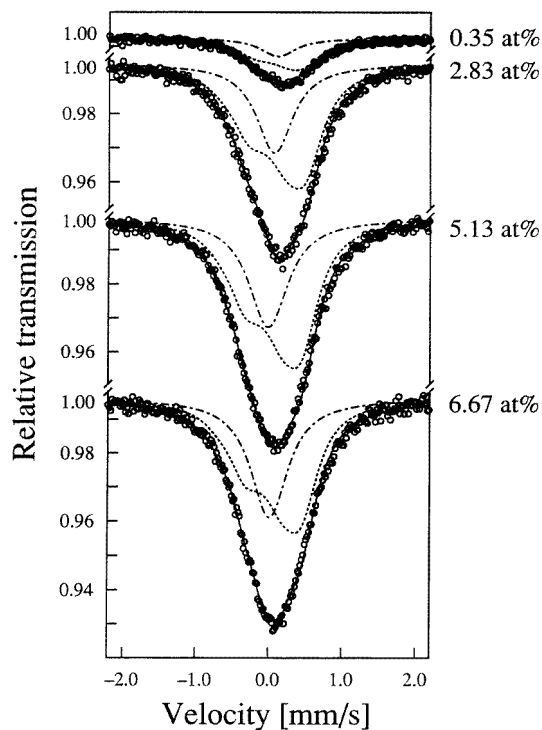


Figure 2. The Mössbauer spectra taken as a function of Kr concentration.

associated with a single Kr atom (monomer) in a-Si [1].

For compact Kr clusters, a ‘bulk’ fraction of 30–40% suggests a cluster size of 1.5–2 nm if we assume that all Kr atoms in the outer layer contribute in the same way to the interface component, and all ‘inner’ Kr atoms contribute to the single line. This size is about a factor of two larger than the upper limit (1 nm) found from the HREM experiments [2]. This discrepancy indicates that the model used to fit the data is too simple. In fact we expect a large number of different environments for Kr atoms in the interface with a-Si. Some of them may have smaller electric field gradients (EFGs) and they may contribute to the broadened single line.

Another parameter which can lead to a broadening of the linewidth of the resonance curve and to a decrease of the transmission of resonant radiation is the Mössbauer thickness. This is directly related to the number of the Mössbauer atoms per cm^2 in the absorber and the absorber recoilless fraction. The Mössbauer thicknesses (at 4.2 K) of the samples analysed range between 0.3 and 5.7, implying that an observable broadening can occur. Furthermore, a saturation of the total intensity of the Mössbauer effect can be seen for the samples containing 5.13 at.% and 6.67 at.% Kr.

The isomer shifts (versus solid Kr at 1 bar) of both the single line and the quadrupole component are plotted against the Kr concentration in figure 4. Both quantities show a decrease for increasing Kr content, which is consistent with the idea that for higher Kr concentration larger precipitates are formed in which the local pressure is smaller. In the case of Kr clusters in an Al host an isomer shift of $0.105(3) \text{ mm s}^{-1}$ (versus solid Kr at 1 bar) has been measured. Because all of the values of the isomer shifts are expressed relatively to

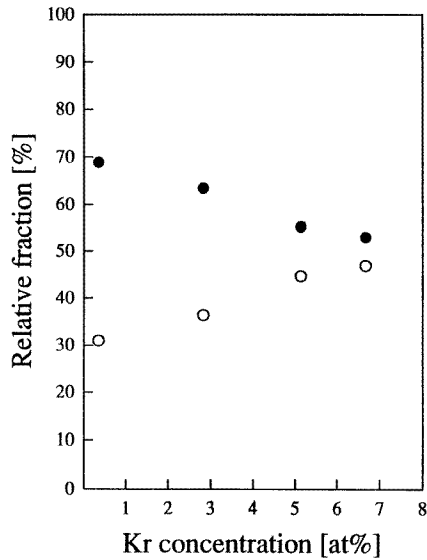


Figure 3. The relative fractions of the single line (○) and the quadrupole component (●) as obtained from the fit for different Kr concentrations.

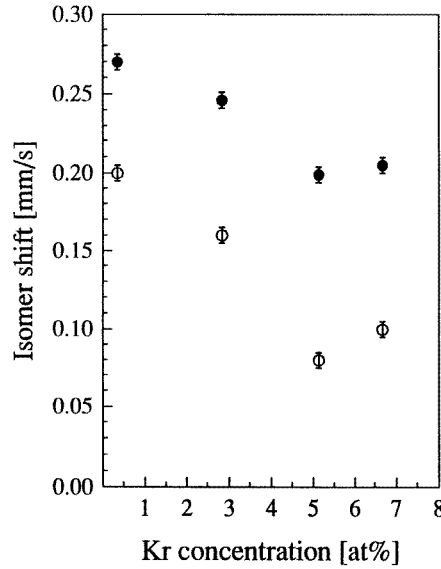


Figure 4. The isomer shifts of the single line (○) and the quadrupole component (●) as functions of the Kr concentration.

those of solid Kr it is possible to compare their values in order to derive conclusions about the pressure in the clusters. For the lowest Kr concentration the isomer shift of the single line is 2.4 times as large as in the case of the Al host [3], for which a Kr molar volume of $23 \text{ cm}^3 \text{ mol}^{-1}$ and a precipitate pressure of 2 GPa at room temperature was derived. We cannot reliably estimate the pressure in the present case, because the isomer shift–pressure relation for ^{83}Kr is not known. For the 5–7 at.% Kr samples the isomer shift is roughly 30% larger than in the case of KrAl, so we expect the pressure to be somewhat larger than 2 GPa. This compares well with an estimate of the pressure in a 5 at.% Kr–Si film on a Si substrate, based on a measurement of the stress in the film: $p = 2.6 \text{ GPa}$ [1, 4].

Because of the large Mössbauer thickness a more careful analysis of the spectra taken as a function of temperature is required. In the case of a single-line absorber, the area of a Mössbauer spectrum can be expressed as

$$A = (\Gamma_a/2) f_s F(t_a) \quad (1)$$

where Γ_a is the absorber contribution to the line width for an infinitely thin absorber, f_s the recoilless fraction in the source and

$$F(t_a) = \pi t_a \exp(-t_a/2) (I_0(t_a/2) + I_1(t_a/2)) \quad (2)$$

with t_a the Mössbauer thickness, and I_0 and I_1 the zeroth- and first-order modified Bessel functions. The Mössbauer thickness

$$t_a = f_a N_a \sigma_0 (\Gamma_n / \Gamma_a) \quad (3)$$

is a function of the recoilless fraction in the absorber f_a , the number of Mössbauer atoms per cm^2 N_a , the resonant absorption cross section σ_0 , the natural linewidth of the emission spectrum Γ_n , and Γ_a .

Figure 5 shows spectra taken at different absorber temperatures for the sample containing 2.8 at.% Kr. The single-line areas of the spectra are plotted versus the temperature in

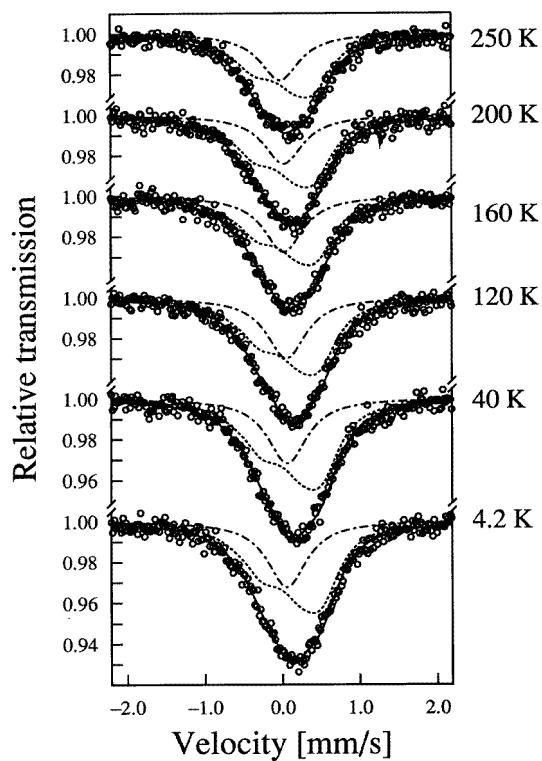


Figure 5. Mössbauer spectra of the 2.83 at.% Kr sample taken at the temperatures indicated.

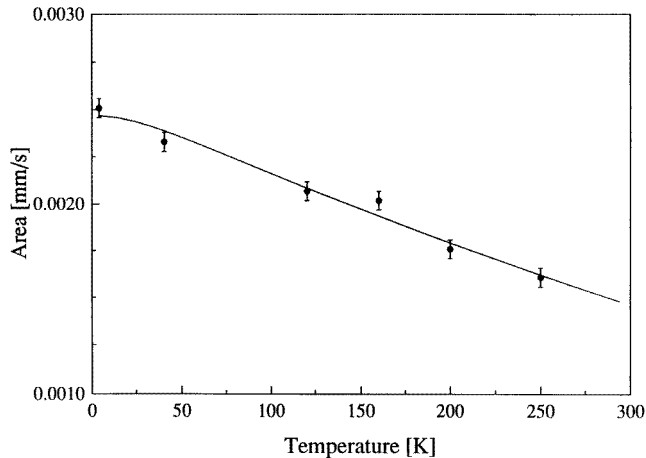


Figure 6. The fit of the single-line areas (\bullet) according to equation (1), yielding a Debye temperature of 116(4) K.

figure 6. The full curve is a fit according to the dependence expressed in (1). The absorber contribution to the linewidth is expected to lie between 0.1 and 0.2 mm s⁻¹. Lower and upper limits for the Debye temperatures corresponding to values of the Γ_a ranging from 0.1

to 0.2 mm s^{-1} are 112(2) and 120(3) K. Therefore, the average Debye temperature becomes $\Theta_M^S = 116(4) \text{ K}$.

Although the value of the Debye temperature for the single line is a factor of two higher than for solid Kr at low temperatures and pressures ($\Theta_M = 64 \text{ K}$), it is not as high as reported in [1]. Apparently the authors underestimated the errors associated with a varying peak/background ratio.

Assuming again that the single-line fraction is associated with ‘bulk’ Kr under pressure, we can derive the Kr molar volume with the aid of the following relation:

$$\Theta_M = \Theta_0 e^{\gamma(1-V/V_0)} \quad (4)$$

where $\Theta_0 = 51.6(5) \text{ K}$, $V_0 = 29.9 \text{ cm}^3 \text{ mol}^{-1}$ and $\gamma = 2.27$ are respectively the Debye temperature, the molar volume and the Grüneisen constant for Kr at 1 bar and at the melting point (see [3] for details). The resulting molar volume is $V_m = 19.2(4) \text{ cm}^3 \text{ mol}^{-1}$. Using the equation of state derived by Polian *et al* [5] it leads to a room temperature pressure of 4.7(4) GPa in the Kr precipitates. This is a factor of two higher than the value quoted earlier for the samples with 5–7 at.% Kr. Roughly the same factor is observed in the behaviour of the isomer shift. The value of 4.7(4) GPa is somewhat higher than the yield stress ($\sigma_y = 3.9 \text{ GPa}$) measured for the a-Si samples [1]. In view of the simplicity of the model the agreement is reasonable.

It is also worthwhile to mention that atomistic simulations yield an effective Debye temperature of $\sim 150 \text{ K}$ for Kr trimers in a-Si [1]. We conclude that although the assumption that the single line is associated with Kr atoms behaving as pressurized bulk Kr is simple, it gives consistent results for the pressure in the precipitates, though it cannot account for their size.

4. Conclusions

a-Si thin films containing Kr in concentrations up to 7 at.% deposited on a Be substrate have been prepared by plasma sputter deposition. ^{83}Kr Mössbauer spectra of these films are fitted with a single line and a quadrupole component, with the single-line intensity increasing with increasing Kr concentration. The quadrupole-split component is associated with Kr atoms at the interface, where the local environment of the Kr atoms gives rise to an appreciable electric field gradient (EFG). Association of the single line with Kr atoms in the interior of a Kr precipitate leads to a precipitate size of $\sim 1.5 \text{ nm}$, which is somewhat larger than the upper limit derived from HREM images (1 nm). Thus it seems that a proportion of the Kr atoms at the Kr–Si interface contribute to the single-line component. An association of the single line with isolated Kr atoms in Si (monomers) can be excluded.

The isomer shift of both components suggests a larger compression of the precipitates than in the case of the Al host. The molar volume increases and the pressure decreases as a function of the Kr concentration. For the 5–7 at.% Kr samples the pressure estimated from the isomer shift compares well with that found from stress measurements.

Temperature-dependent measurements on a 2.8 at.% Kr sample could be fitted with the Debye model, yielding a characteristic temperature of 116(4) K for the single-line component. The corresponding pressure of 4.7(4) GPa is a factor of two higher than that estimated for the 5–7 at.% samples [1]. The results show that krypton incorporated in amorphous Si resides in small precipitates, with a pressure limited by the yield stress of the host material.

Acknowledgments

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