# Characteristic and noncharacteristic x rays produced during 1-MeV argon bombardment of silicon

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This work reports the first detailed examination of the noncharacteristic x-ray distribution produced during 1- MeV Ar bombardment of silicon. A crystal spectrometer was used to observe the characteristic and noncharacteristic x rays. It is shown that to within 5 eV the noncharacteristic x-ray band is continuous and tails off in the region of 1.4 keV, as required by the molecular x-ray interpretation. We have obtained the true shape of the noncharacteristic x-ray band in the energy range 675–1550 keV by using a rubidium acid phthalate crystal spectrometer calibrated for its relative efficiency. The observation of a broadened argon $L$ line spectrum and multiple satellite line in the Si $K$ spectrum shows that a high degree of excitation is produced in the $L$ shells of both argon and silicon during the collision.

During the past three years, several groups have reported the observation of noncharacteristic x rays when solid silicon is bombarded by argon ions with energy greater than ~150 keV.[1-4] Saris *et al.*[1] first interpreted the noncharacteristic x rays as arising from the radiative filling of a dynamic $2p\pi$ Ar-Ar molecular orbital during the collision of an incident Ar ion and an implanted argon atom in the silicon crystal. Further examples of similar molecular-type x rays have also been reported,[5-8] and interest in the subject is growing rapidly.

However, no measurements of the noncharacteristic band have been made with sufficient spectral resolution to determine whether the band consists of a series of lines or is actually continuous. We report here the first such high-resolution (5 eV) measurements.

Two difficulties[9] associated with the molecular x-ray interpretation have been clarified in recent work. First, the molecular x-ray mechanism should not give a peak in the spectral distribution, as observed initially by Saris *et al.*[1] Rather, calculations by Briggs[10,11] have shown that the molecular x ray for $K$ shells yields a spectral distribution which decreases monotonically with energy and drops off rapidly beyond the united atom limit. Although similar calculations have not been reported for $L$ shells, peaks in the spectrum are expected only for collisions at specific impact parameters.[12] The peak seen by Saris *et al.* has been attributed to varying absorption in the detector windows.[2,10,13] Unknown impurities represent an alternative, but much less likely explanation, which can only be tested definitively by looking for line structure in the molecular x-ray distribution with a high-resolution spectrometer. A second problem, which arises from assigning the origin of the x rays to Ar → Ar interactions, is that the implanted argon density is not high enough for the necessary double collision (one collision to create a $2p$ vacancy, and a second to broaden the Ar $L$ line asymmetrically towards the high-energy side) to be sufficiently probable to account for the observed intensity. This does not constitute a serious objection to the molecular x-ray interpretation as such, since the x ray could be emitted during an Ar → Si collision. Indeed Bissinger and Feldman[2] have shown that at low doses, the band is due almost entirely to Ar → Si collisions.

The chief reason for attributing the molecular x ray to Ar → Ar rather than Ar → Si collisions was an observed increase in yield with argon dose. However, since there must be a $2p$ vacancy in the argon projectile in order to produce both the Si $K$ x ray[15] and the molecular x ray, and since such vacancies are generated more copiously in Ar → Ar collisions than in Ar → Si collisions, the dose dependence could arise because the equilibrium population of the argon beam ions with $2p$ vacancies increases with argon buildup in the solid; the number of molecular x rays would then increase proportionally. This in turn is also consistent with a simultaneous increase in Si $K$ x-ray yield, as reported by Cairns *et al.*[3] They showed also that increasing the $2p$ vacancy production by bombarding silicon carbide rather than silicon generated copious yields of both molecular x rays and Si $K$ x rays. Admittedly, MacDonald and Brown's observation[5] of noncharacteristic x rays from argon-ion collisions with solid argon supports the basic idea of the molecular x-ray

mechanism operating in Ar → Ar collisions in dense targets, but their reported frequency distribution apparently differs from the Ar → Si spectrum: their distribution tails off to 1800 eV, which is near the krypton united-atom $L$ x-ray energy, in agreement with predictions for Ar → Ar collisions. Similar conclusions are indicated by Bissinger and Feldman's high-argon-dose results.[2]

Thus, it becomes apparent that high-resolution measurements of the type reported here, determining the molecular x-ray spectrum end point more accurately, should distinguish the Ar → Ar united-atom limit (~1800 eV) from the Ar → Si limit (~1400 eV) when calculations of the molecular x-ray spectra for $L$ shells become available. It should be stressed that since there are as yet no theoretical predictions for the shape of the band near the united-atom limit in the case of $L$-shell x rays, conclusions based on such observations must at present be rather tentative. In this paper, we report high-resolution x-ray measurements, made with a crystal spectrometer, of the x rays within the 200–2000-eV energy range excited by 1-MeV argon ions in solid silicon.

These studies were conducted using the IBM 3.2-MeV accelerator. The x rays were resolved by means of a curved crystal spectrometer containing a gas-flow proportional counter fitted with a 1-$\mu$m polypropylene window. The results presented here have been corrected for the variation in solid angle which occurs as the spectrometer is scanned through the energy range of each crystal. In addition, in order to extract the true shape of the noncharacteristic x-ray band from the observed shape, it is necessary to take into account (i) variations in crystal diffraction efficiency versus wavelength, and (ii) variations in mass-absorption coefficient of the proportional counter window versus wavelength. This was done as follows: A Si(Li) detector with a 9-$\mu$m Be window was calibrated in the low-energy region by using published absolute yield values for proton excitation of Cu $L$, Mg $K$, and Al $K$ x rays.[14] With this calibrated Si(Li) detector, we were able to measure the relative efficiency of the combined RAP crystal and flow proportional counter spectrometer system as a function of energy in the 675–1500-eV region. [Below 675 eV, the Si(Li) calibration becomes too uncertain.]

The lower curve in Fig. 1 displays the x-ray yield in the region from 523 to 1560 eV produced by 1-MeV argon-ion bombardment of silicon, showing that the noncharacteristic x rays consist of a broad band, essentially free from any well-defined structure, and apparently tailing off at ~1.4 keV. Superimposed on this band are the second-order Si $K$ x-ray lines which serve to show the resolution of the crystal spectrometer in this energy interval (<5 eV). The tailing off at ~1.4 keV suggests Ar → Si collisions as the source of these x rays, since 1-MeV argon ions can penetrate to the united-atom limit in either Ar → Si or Ar → Ar collisions. (Note that in this figure, as in the others to be referred to, the channels are in equal-wavelength increments, as is customary with crystal spectrometer spectra, rather than equal-energy increments.)

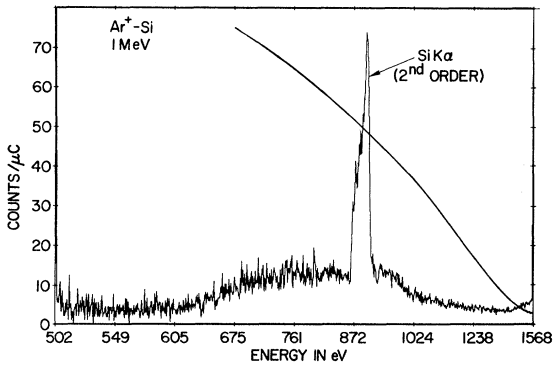


FIG. 1. Noncharacteristic x-ray band generated during 1-MeV $Ar^+$ bombardment of silicon (lower jagged solid curve). The Si $K$ x-rays which are also produced during the collisions (see Fig. 3) appear in the region of the spectrum as a second-order effect and serve to demonstrate the energy resolution of the spectrometer. The upper smooth curve shows RAP data corrected for spectrometer efficiency and the scattering of Si $K$ into the detector at the high-energy end of the spectrum (dotted region). Crystal: RAP (Rubidium acid phthalate).

The upper curve in Fig. 1 shows rubidium acid phthalate (RAP) data corrected for overall spectrometer efficiency. This curve demonstrates that the molecular x-ray yield increases monotonically toward low energies and tails off near 1400 eV but does have some intensity above the united-atom limit, as predicted by Briggs and Macek.[10,11]

The data in Fig. 1 must also be corrected at the high-energy end for Si $K$ x rays which somehow reach the detector (because of the intense primary Si $K$ yield). This was evaluated by introducing an Al filter (which selectively absorbs Si $K$ radiation) and comparing the yield with and without the filter. Up to 1250 eV, less than 5% of the yield was from Si $K$. At 1500 eV, about 80% of the yield comes from Si $K$ x rays. The upper curve includes a correction to eliminate counts due to Si $K$ x rays.

The degree of excitation of the argon projectile is very relevant, and may be deduced from its x ray spectrum. Thus, Fig. 2 shows that the Ar $L$ x-ray region displays a peak which occurs at a higher energy than the normal value of 220 eV. The energy resolution of the spectrometer in this

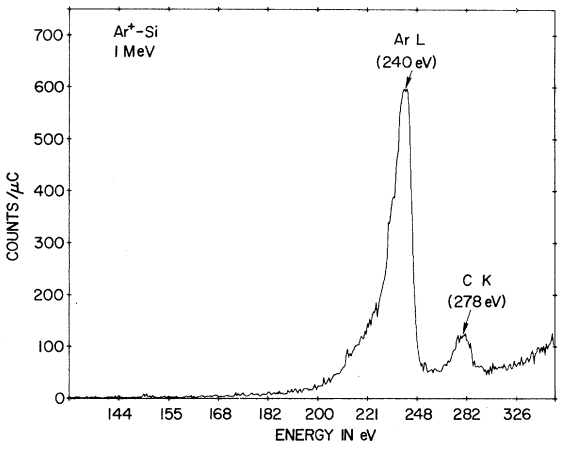


FIG. 2. Ar $L$ x-ray spectrum produced during 1-MeV $Ar^+$ bombardment of silicon. The Ar $L$ line has been displaced from its expected position at 220 to 240 eV and is broadened considerably. The resolution of the spectrometer in this region of the spectrum is estimated to be 5 eV. Crystal: LSD (Lead stearate decanoate).

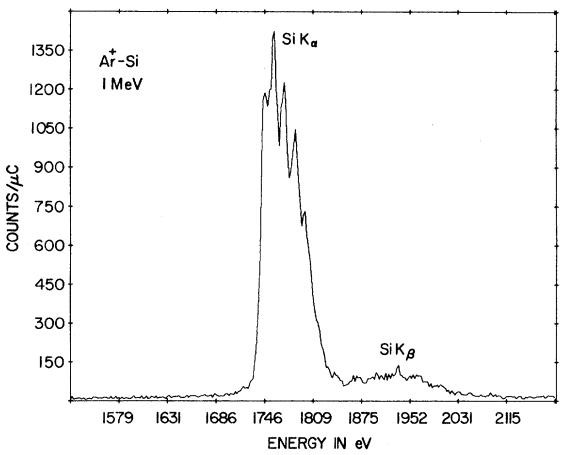


FIG. 3. Si $K$ x-ray spectrum produced by 1-MeV $Ar^+$ bombardment of silicon. Crystal: ADP (Ammonium dihydrogen phosphate).

region is 5 eV. The rather broad energy distribution of the Ar $L$ line may represent a whole series of lines from argon in various states of excitation. The peak of 240 eV *could* be accounted for simply by loss of $3p$ valence electrons, since Garcia *et al.*[16] show that loss of *all* of these electrons would shift the line to ~255 eV. Note, however, that the Fano-Lichten model predicts that $2p$ vacancy production would certainly be accompanied by $3p$ vacancy production so that the peak shift to 240 eV must be partly due to $3p$ vacancies. In addition, we would expect the Ar $L$ line to be collision broadened as the emitting ion travels through the solid. This should occur because since the average silicon internuclear spacing is ~2.5 Å, the argon ion can never be further than ~1.3 Å from a silicon atom, and so perturbations by the nearby silicon atoms will depress the $2p$ level somewhat and perturb the upper $3s$ level. In fact, one may in a sense regard *the entire band* between the Ar $L$ x ray and the Ge $L$ x ray limit as collision broadened and shifted Ar → Si molecular x rays.

In contrast to the Ar $L$ case, Fig. 3 shows that Si $K$ x rays produced during 1 MeV argon bombardment of silicon exhibit no obvious collision broadening, although the x rays could be shifted to higher or lower frequency by collisions between recoil silicon and silicon atoms in the target. The $1\sigma_g$ $Si_2$ orbital gives rise to a high-frequency shift; the $1\sigma_u$, to a low-frequency shift. The satellites shown here are evidence of excitation of the silicon, being due to various degrees of silicon $2p$-vacancy production and are similar to the aluminum satellites observed by Knudson *et al.*[17]

It will be noted that the relative intensities of the satellites in Fig. 3 are not reproduced in the second-order spectrum shown in Fig. 1. As a check on this, a series of primary targets having characteristic x rays in the region of silicon $K$ and its satellites were bombarded in the electron microprobe, and the relative intensities of the x rays, as detected with an ADP crystal, were noted. These x rays were then detected in second order with an RAP crystal, and the relative intensities were found to alter in a similar manner to the differences shown in Figs. 1 and 3. This effect is thought to be due most likely to the x rays in question being close in energy to the rubidium $L_3$ absorption edge (1807 eV) of the RAP crystal.

Our conclusions may be summarized as follows. The lack of structure in the 1000-eV x-ray-energy region rules out unknown line sources as the origin of the noncharacteristic x rays and lends strong support to the molecular interpretation. The endpoint energy suggests that the transitions take place during the lifetime of the Ar-Si pseudomolecule, rather than the Ar-Ar pseudomolecular, as was originally proposed. The broadening of the Ar $L$ is taken as evidence of a collision broadening effect which extends also to the noncharacteristic x-ray band. In contrast, the Si $K$ x rays are not broadened, although they do exhibit multiple-excitation effects.

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