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THERMAL STABILITY OF AMORPHOUS Ta–Ir BETWEEN Y–Ba–Cu–O AND SILICON*

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Summary

Amorphous buffer layers of Ta–Ir, sandwiched between Y–Ba–Cu–O thin films and Si(100) substrates, prevent interface reactions during annealing in oxygen ambient up to 800 °C. Above 650 °C, amorphous Ta–Ir–O, which is formed during annealing, crystallizes into Ta_2O_5 and IrO_2, and pinholes in the Y–Ba–Cu–O film and buffer layer are observed. Reaction with silicon does not occur after annealing up to 900 °C.

The relatively high sintering temperatures needed to obtain high T_c superconducting materials are a drawback for their application, especially in thin film form. For many electronic applications silicon would be an interesting substrate. The use of superconducting thin films as interconnects, or the combination of superconducting and microelectronic devices on a single chip, will require stable interfaces with silicon. However, silicon reacts readily with Y–Ba–Cu–O at high processing temperatures [1 - 3]. Above 400 °C a buffer layer between Y–Ba–Cu–O and silicon is needed. Because of the absence of grain boundaries, amorphous thin films could be ideal diffusion barriers, if their crystallization and reaction temperatures are sufficiently high.

The amorphous alloy $Ta_{55}Ir_{45}$ (a-$Ta_{55}Tr_{45}$) is at present the alloy with the highest reported crystallization temperature of 1010 °C [4]. In thin film form a-$Ta_{55}Ir_{45}$ has been found to be stable up to 900 °C [5, 6]. Furthermore, reaction between a-$Ta_{55}Ir_{45}$ and silicon in vacuum takes place between 850 and 900 °C [7], which is also the highest reported reaction temperature with silicon. Therefore, a-TaIr is a possible candidate as a buffer layer be-

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tween Y–Ba–Cu–O and silicon. The thermal stability of a-TaIr, sandwiched between Y–Ba–Cu–O and silicon, has been the subject of our investigation on which we report here.

Two types of experiments are performed. First, amorphous $Ta_{55}Ir_{45}$ layers of 2000 Å thickness are deposited by dual electron gun evaporation in a base vacuum better than 5×10^{-6} Pa onto Si(100) substrates. The silicon substrates are covered with a native oxide. For the second type of sample, a thin film of Y–Ba–Cu–O with a thickness of approximately 1 μm is deposited onto the Si/a-TaIr samples, at a substrate temperature of 400 °C, by a laser ablation technique as described by Dijkkamp *et al.* [8]. In order to obtain high T_c superconductivity, it is necessary to anneal the as-deposited film in an oxygen ambient. Therefore, both types of samples are isochronically annealed for 30 min in oxygen flow at temperatures between 500 and 900 °C. Analysis of the samples is carried out by X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS) and scanning electron microscopy (SEM).

RBS results for the Si/a-TaIr samples are presented in Fig. 1. The spectrum of the as-deposited sample shows that at the surface only tantalum and iridium are observed. After heating for 30 min at 500 °C in an oxygen flow, the effect of reaction with O_2 is seen: the yield of the back-scattered particles from the surface of the Ta–Ir layer has decreased and the Ta–Ir signal is broader. In the RBS spectrum oxygen is observed at the sample surface. Furthermore, as a result of additional stopping of oxygen, which is clearly penetrating into the amorphous Ta–Ir top layer, the silicon signal is shifted to lower energies. The trailing edge of the Ta–Ir signal and the front edge of the silicon signal are as steep as in the spectrum of the as-

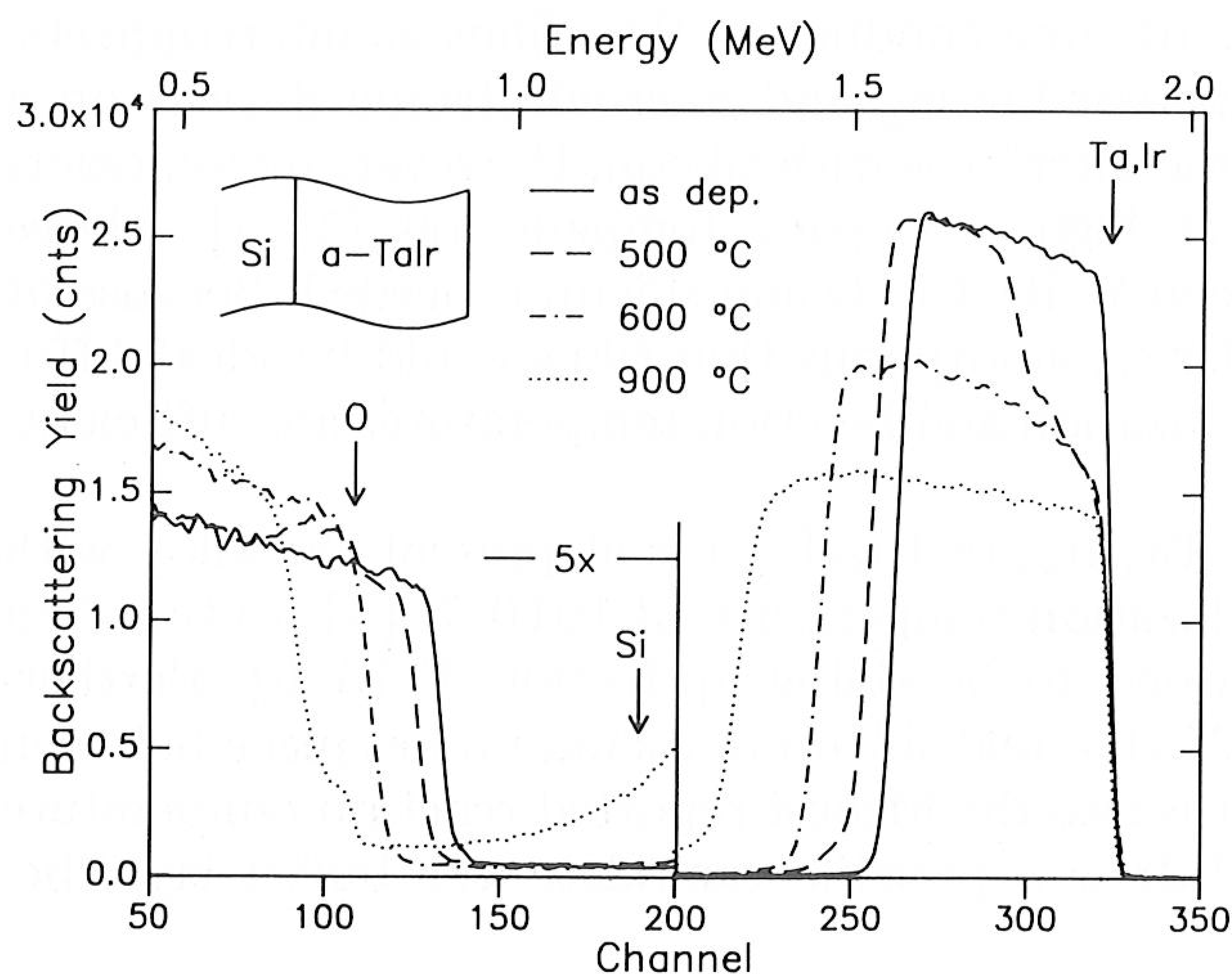

Fig. 1. RBS spectra of the Si/a-TaIr samples. Samples are heated for 30 min in an oxygen flow at the temperatures indicated. The structure of the as-deposited sample is also shown.

deposited sample, indicating that there still is a sharply defined interface between the silicon substrate and Ta–Ir overlayer. After heating for 30 min at 600 ℃, oxygen is mixed completely through the Ta–Ir layer. Intermixing with the silicon substrate is not seen. The silicon signal is shifted to lower energies and there is no evidence for silicon at the sample surface. After heating for 30 min at 900 ℃, even more oxygen is taken up into the Ta–Ir layer, whereas the interface at the silicon substrate remains unaffected. SEM, however, shows the formation of pinholes and local swelling of the film.

In Fig. 2, spectrum a, the XRD spectrum of the as-deposited amorphous Ta–Ir is depicted. No other phases are detected. After heating for 30 min at 650 ℃ in an oxygen flow (Fig. 2, spectrum b), the top of the amorphous Ta–Ir peak is shifted from 40.0° to 40.8° in 2θ, which indicates a shift of the interatomic distances from 2.25 to 2.21 Å. In addition, the width of the amorphous Ta–Ir signal is narrower, indicating a higher degree of order. This is caused by oxygen incorporation in the Ta–Ir layer. At lower angles, another amorphous phase is observed. This must be amorphous Ta–Ir–O, or a mixture of amorphous Ta–O and Ir–O, formed during the anneal. Also, the first traces of crystalline Ta_2O_5 are observed. After the heat treatment at 900 ℃ (Fig. 2, spectrum c) the amorphous phases have almost completely crystallized. All the peaks could be assigned to Ta_2O_5 and IrO_2. No other phases are observed, which indicates that silicon is not taking part in any

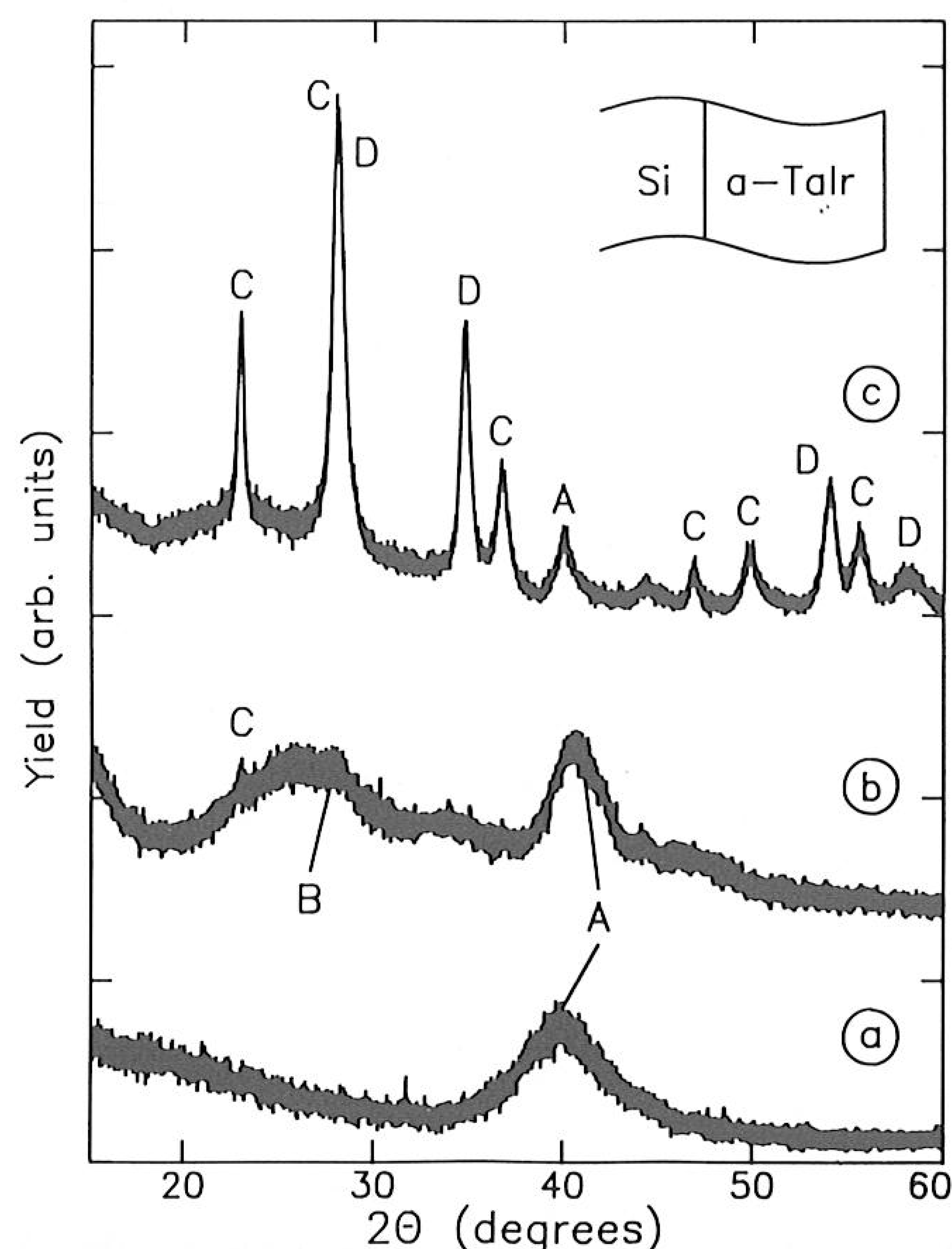

Fig. 2. XRD data of the Si/a-TaIr samples: spectrum a, as-deposited amorphous Ta–Ir (A) on an Si(100) single crystal; spectrum b, after heating for 30 min at 650 ℃ in an oxygen flow; observed are amorphous Ta–Ir (A), amorphous Ta–Ir–O (B), which is formed during annealing, and the beginning of amorphous Ta–Ir–O crystallization into Ta_2O_5 (C); spectrum c, almost fully crystallized a-TaIr (A) after heating for 30 min at 900 ℃ in O_2; all the peaks can be identified as Ta_2O_5 (C) and IrO_2 (D).

reaction with the overlayer. Formation of SiO_2 at the silicon substrate will be restricted to very thin layers. Dry oxidation of Si(100) single crystals, for an oxidation time of 1 h at 900 °C in atmospheric oxygen ambient, gives rise to the formation of an amorphous SiO_2 layer of approximately 100 Å thickness [9]. Although, as a result of a continuous supply of oxygen through the Ta–Ir–O film, the formation of a thin layer of amorphous SiO_2 at the higher annealing temperatures is likely, such a thin amorphous layer, covered by tantalum and iridium, escapes detection by RBS or XRD.

The XRD data of the Si/a-TaIr/Y–Ba–Cu–O samples (Fig. 3) show the same behaviour as the data of the Si/a-TaIr samples. Figure 3, spectrum a, shows the diffraction pattern of an as-deposited sample. The Y–Ba–Cu–O layer, which is deposited in vacuum onto Si/a-TaIr substrates at 400 °C, is amorphous [8, 10]. The diffraction feature of Y–Ba–Cu–O in the XRD spectrum is very broad (2θ approximately between 10° and 30°) and of very low intensity. Amorphous Ta–Ir is observed, and also some $BaCO_3$. After heating in an oxygen flow for 30 min at 600 °C (Fig. 3, spectrum b) the amorphous Ta–Ir and Ta–Ir–O phases and some crystalline Ta_2O_5 are observed, as in the Si/a-TaIr samples. Apparently, oxygen is supplied to the Ta–Ir buffer layer through, or from, the Y–Ba–Cu–O top layer during the anneal. Furthermore, a larger amount of crystalline $BaCO_3$ is observed. There is no evidence for other phases. After annealing at 800 °C (Fig. 3, spec-

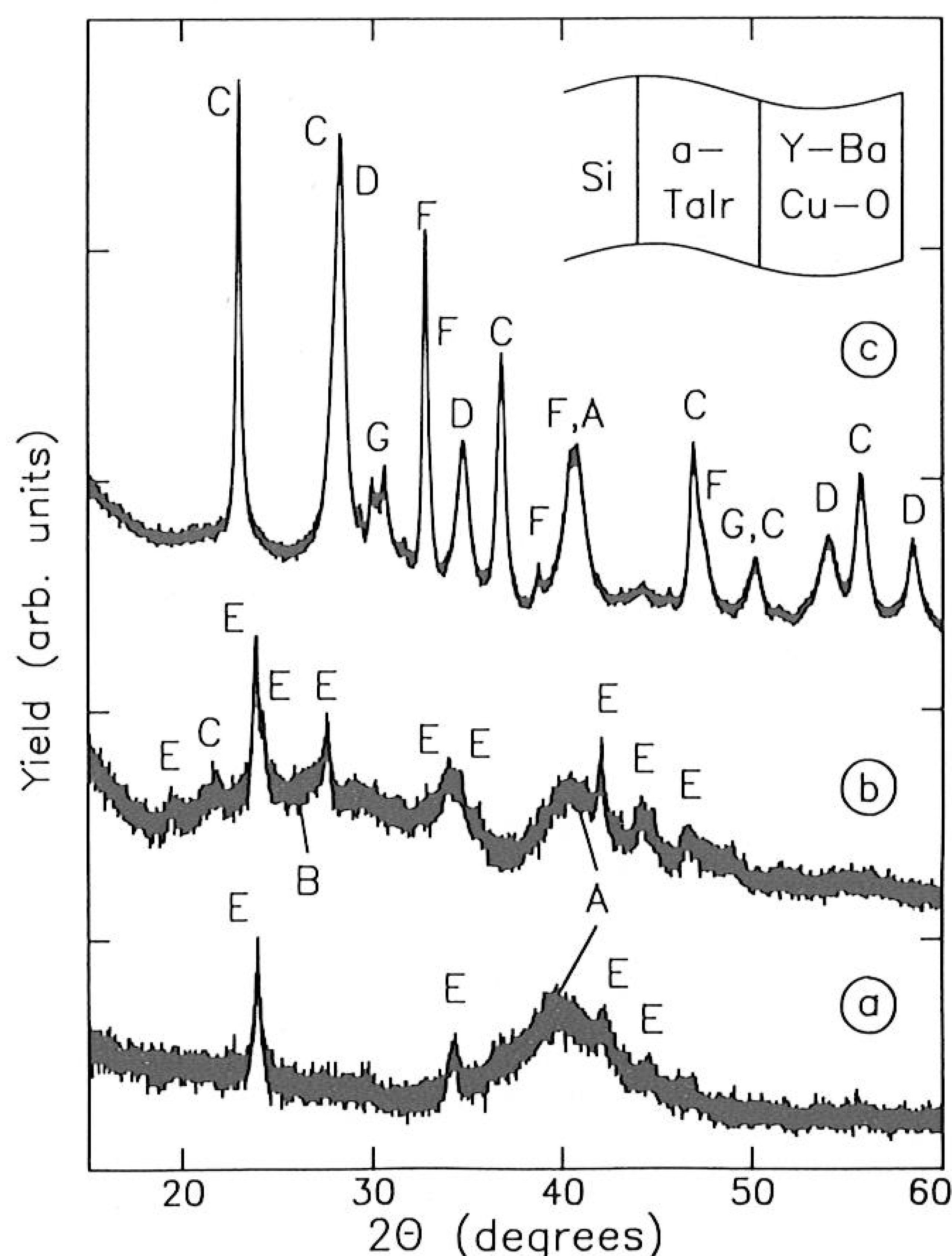

Fig. 3. XRD data of the Si/a-TaIr/Y–Ba–Cu–O samples: spectrum a, amorphous Ta–Ir (A) and some crystalline $BaCO_3$ (E) after depositing the Y–Ba–Cu–O at a 400 °C substrate temperature; spectrum b, after heating for 30 min at 600 °C in an oxygen flow; observed are amorphous Ta–Ir (A) and Ta–Ir–O (B), and crystalline $BaCO_3$ (E); spectrum c, after heating for 30 min at 800 °C in an oxygen flow; the amorphous Ta–Ir–O has crystallized into Ta_2O_5 (C) and IrO_2 (D); the $BaCO_3$ has completely disappeared, and some $YBa_2Cu_3O_{6+\delta}$ (F) and a mixture of Y_2BaCuO_5 and $BaCuO_2$ (G) are observed.

trum c) the amorphous phases have crystallized and Ta_2O_5 and IrO_2 have been formed. Also, the $BaCO_3$, which decomposes at this temperature, has disappeared. As shown in the XRD spectra, the released barium combines with the other constituents of the Y–Ba–Cu–O layer, and the supplied extra oxygen, to form a fine-grained $YBa_2Cu_3O_{6+\delta}$ phase. Furthermore, some low intensity peaks are observed, which are identified as the Y_2BaCuO_5 and $BaCuO_2$ phases. There is no evidence for formation of silicides. After annealing at 900 °C, some unidentified peaks are observed which cannot be assigned to any known silicides and are probably due to reactions between the various oxides.

In Fig. 4 RBS spectra of Si/a-TaIr/Y–Ba–Cu–O samples, isochronically annealed for 30 min at 600 and 700 °C in an oxygen flow, are shown. The spectrum of the sample annealed at 600 °C shows barium, yttrium, copper and oxygen at the surface. The Ta–Ir peak is not seen at the surface but is shifted to lower energies. Reaction with oxygen has already taken place at this temperature, as shown by the XRD experiments, and there is no evidence that intermixing of the Y–Ba–Cu–O and Ta–Ir layers, or substrate, has occurred. After annealing at 700 °C, however, tantalum and/or iridium appears at the sample surface. This is caused by the formation of pinholes and cracks in the Y–Ba–Cu–O top layer and the Ta–Ir buffer layer, as confirmed by SEM. Although intermixing of the Ta–Ir and Y–Ba–Cu–O layers cannot be excluded, silicon is not observed to appear at the sample surface. Also, after annealing in an oxygen flow up to 900 °C, there is no evidence for silicide formation.

In summary, we have found that amorphous Ta–Ir reacts with O_2 at temperatures of 500 °C or higher. Below an annealing temperature of 650 °C,

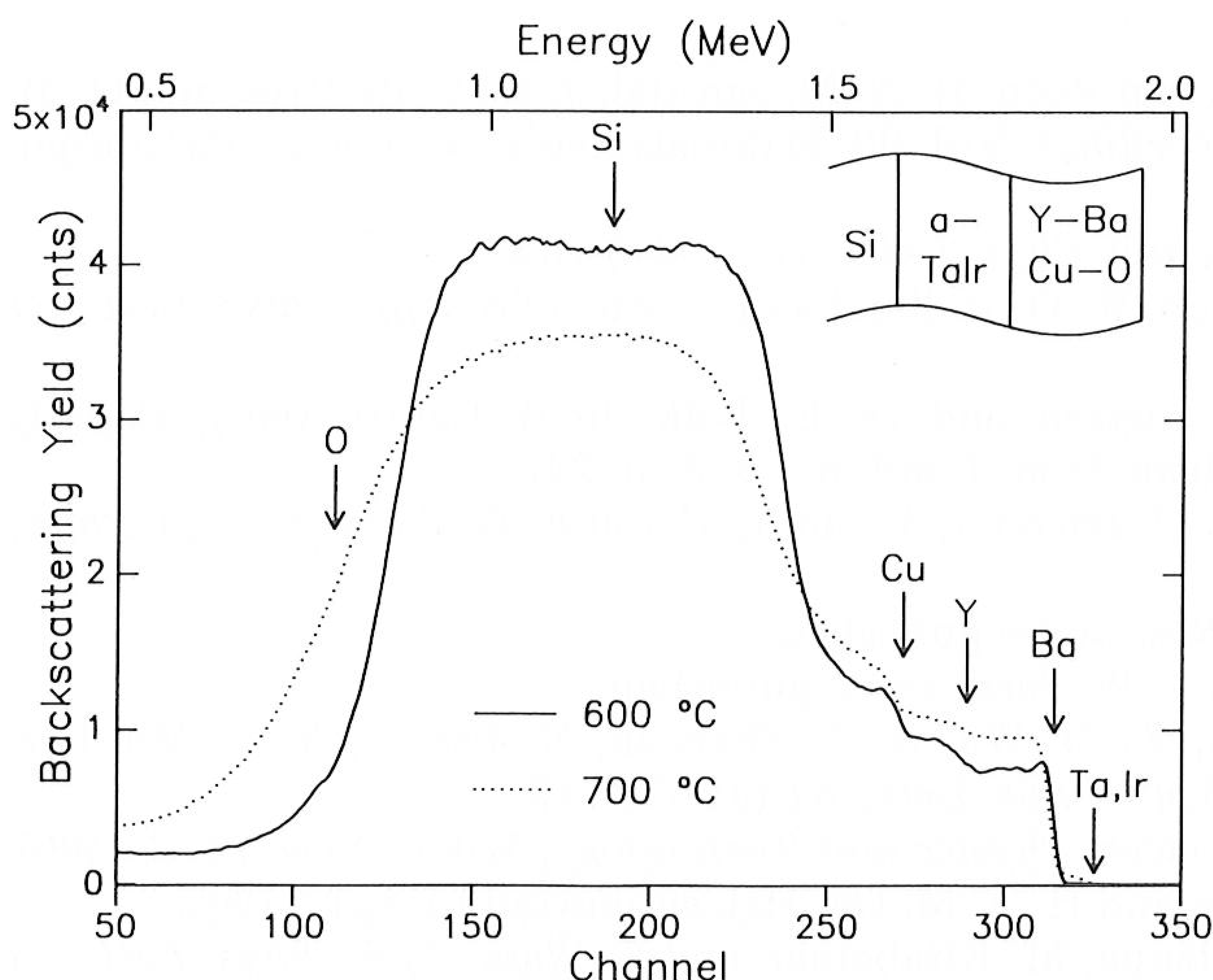

Fig. 4. RBS spectra of Si/a-TaIr/Y–Ba–Cu–O samples after sintering for 30 min at 600 and 700 °C in an oxygen flow, the temperature region in which the formation of pinholes starts. The structure of the as-deposited sample is also shown.

amorphous Ta–Ir–O compositions are formed. Above this temperature, the amorphous oxide crystallizes into Ta_2O_5 and IrO_2. If we use a-TaIr as a buffer layer between silicon substrates and Y–Ba–Cu–O top layers, oxygen diffused through, or supplied from the Y–Ba–Cu–O layer reacts with the Ta–Ir buffer layer in a rather similar fashion. As soon as the amorphous buffer layer crystallizes, pinholes and cracks are formed in both the buffer layer and the Y–Ba–Cu–O film. Some $YBa_2Cu_3O_{6+\delta}$ is formed after annealing at 800 °C in an oxygen flow. In all cases, there is no evidence for reaction with silicon after annealing in an oxygen flow up to 900 °C. Although the crystallization temperature of a-TaIr is approximately 1000 °C in vacuum, during annealing in an oxygen ambient amorphous Ta–Ir–O is formed, which crystallizes at 650 °C. Amorphous Ta–Ir is an effective barrier against interdiffusion between Y–Ba–Cu–O and silicon up to at least 900 °C. Amorphous Ta–Ir should be a good candidate as a buffer layer in the case of silicon substrates if the electrical properties of the oxidized layer turn out to be useful and superconducting films are deposited at 650 °C [11, 12].

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