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INVESTIGATIONS OF DEFECTS IN EFG CRYSTALLINE SILICON RIBBONS

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Abstract. This paper describes the structure of EFG silicon ribbons made in Poland. Twin boundaries, twin lamellae, dislocations, and high- and low-angle grain boundaries were found to occur in the crystals obtained. The investigations showed that graphite used for dies was largely responsible for the rise of these defects.

INTRODUCTION

The production of semiconductor elements and devices requires costly and labour-consuming mechanical working involving orientation, cutting and polishing of single crystals. The elimination of these operations in order to simplify the technological process, and thereby to reduce the price of product, demands the development of new methods of production of all kinds of single crystals. Particularly important is to develop a technique of obtaining profiled monocrystals of such materials as silicon, sapphire, and two- or multicomponent semiconductor compounds. Considering their future use, the research and technological works are focussed primarily on growing single crystals in the form of ribbons, plates, fibres and tubes, as well as ones having more complex geometrical shapes.

As a result of extensive studies of the use of photocells for the conversion of solar into electric energy, silicon finds wider and wider application as the basic material employed for their construction (Jakubicki, Kątcki, 1978).

A method showing great promise of mastering the process of crystallization of silicon ribbons, which are used extensively in solar batteries, is the EFG method, introduced in 1971 (La Belle, 1971; Chalmers *et al.*, 1972; Ciszek, 1972), or its modified version CAST (Ciszek, Schwuttke, 1975). Basing on the assumptions

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of the EFG method, the present authors carried out the process of crystallization of silicon ribbons and obtained a dozen or so ribbons. This paper attempts to characterize the structure of the resulting crystals.

METHOD OF CRYSTALLIZATION

The EFG method utilizes the capillary effect which causes liquid silicon in the capillary slot of the die to rise relative to the position of the free surface of liquid silicon in the crucible. The shape and size of the crystallizing ribbon are determined by the outer edges of the upper die surface.

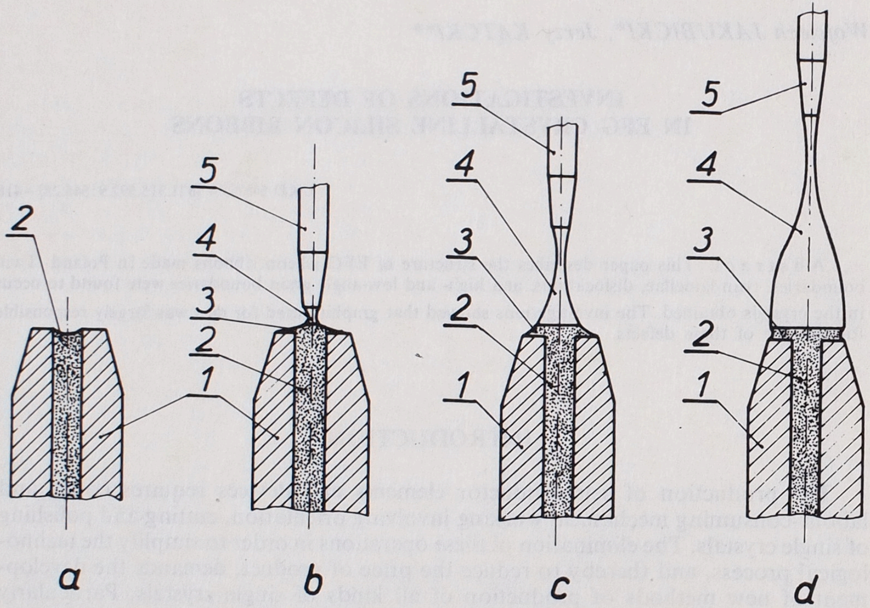

Fig. 1. Initiation of the crystallization of EFG silicon ribbons

1 – die, *2* – capillary filled with liquid silicon, *3* – liquid silicon layer, *4* – crystal, *5* – seed; *a* – filling of the capillary with liquid silicon, *b* – bringing the seed into contact with the liquid silicon layer spread over the die surface, *c* – neck formation, *d* – expansion of the crystal at increasing pulling rate

Fig. 1 shows the initiation and course of the initial stages of ribbon formation. The stage of stable growth (Fig. 1*d*) begins when the liquid silicon layer reaches the outer edges of the die.

GROWTH CONDITIONS AND THE STRUCTURE OF SILICON RIBBONS

The process of growth of silicon ribbons was carried out in a resistance heating crystallizer using Czochralski's method, and in an induction heating crystallizer without crucible, both specially adapted for this purpose. Graphite dies with a capillary slot 0.3 – 1.0 mm in width and 10 – 23 mm in length, and quartz crucibles were used in all the runs. The processes were conducted in the atmosphere of argon. The seeds showed orientation of the *<112>{111}* type. Pulling rate was 0.05 – 13 mm/min.

Microscopic examination of the resulting ribbons revealed the presence of:
- dislocations,
- twin boundaries, twin lamellae,
- high- and low-angle grain boundaries,
- point defects,
- graphite and silicon carbide inclusions.

Phot. 1 shows a fragment of the ribbon surface with visible dislocation pile-ups, dislocation etch pits arranged in lines and twin lamellae. Phot. 2 is a scanning electron micrograph of a fragment of the silicon ribbon fracture and its lateral surface with visible parallel twin boundaries. The position of the twin boundaries shows that the orientation of the ribbon differs from the initial orientation of the seed due to earlier twinning.

The material used for dies affects significantly the structure of ribbons. One of such materials is graphite. Due to the erosive action of liquid silicon on graphite, graphite grains are detached from the capillary surface, becoming inclusions in liquid silicon. As a result of reactive diffusion on the surface of graphite being in contact with liquid silicon, a thin layer of silicon carbide forms at the capillary surface. This layer is also subject to erosion and, in consequence, silicon carbide inclusions get into liquid silicon. It has been found that the graphite and silicon carbide inclusions present in liquid silicon are responsible for the formation of twin lamellae and high-angle grain boundaries in the crystal during its growth (Phot. 3). Small silicon carbide crystals discernible at the ribbon surface (Phot. 4) formed as a result of silicon carbide inclusion getting to the edge of the solidification front. The mechanism of formation of silicon carbide and graphite inclusions and of silicon carbide crystals was discussed in a separate paper (Ciszewski *et al.*, in press).

The generation of transverse twin boundaries in the ribbon results in a change in its initial orientation. This change in orientation is attended by a change in the meniscus angle φ_0, due to which the regular shape of the lateral ribbon surface is disturbed (Phot. 5).

At rapid growth rates (over 10 mm/min.), characteristic ridges form at the ribbon surface (Phot. 6) due to constitutional supercooling taking place under such conditions (Surek *et al.*, 1977).

CONCLUSIONS

This paper is an attempt at characterizing the structure of silicon ribbons obtained by the authors. A relationship has been found to exist between the structure and the conditions of crystallization. The present investigations will serve as a basis for the determination of optimum conditions of production of crystalline silicon ribbons.

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BADANIA DEFEKTÓW MONOKRYSTALICZNYCH TAŚM KRZEMOWYCH OTRZYMANYCH METODĄ EFG

Streszczenie

W artykule dokonano charakterystyki struktury taśm krzemowych otrzymanych metodą EFG w kraju. W uzyskanych kryształach stwierdzono występowanie granic bliźniaczych, lamelli bliźniaczych, dyslokacji, wysoko- i niskokątowych granic ziarn. Na powstawanie wymienionych defektów istotny wpływ ma zastosowanie grafitu jako materiału na matryce.

OBJAŚNIENIE FIGURY

Fig. 1. Zainicjowanie procesu krystalizacji taśm krzemowych metodą EFG
1 – matryca, *2* – kapilara wypełniona ciekłym krzemem, *3* – warstewka ciekłego krzemu, *4* – kryształ, *5* – zarodź; *a* – wypełnienie kapilary ciekłym krzemem, *b* – zetknięcie zarodzi z warstewką ciekłego krzemu, rozlaną na powierzchni matrycy, *c* – utworzenie przewężenia (szyjki), *d* – rozszerzanie się kryształu przy zwiększaniu szybkości wyciągania

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Fragment silnie zdeformowanej struktury taśmy krzemowej
1 – skupienia dyslokacji, *1* – lamelle bliźniacze, *3* – jamki dyslokacyjne ułożone w linie. Pow. 50 ×

Fot. 2. Szereg równoległych, przebiegających wzdłuż kryształu granic bliźniaczych widocznych na przełamie (z lewej) i na powierzchni taśmy (z prawej strony rysunku). SEM. pow. 100 ×

Fot. 3. Lamelle bliźniacze i szereg szerokokątowych granic ziarn powstałe w wyniku obecności wtrącenia grafitu w warstewce ciekłego krzemu. SEM. pow. 260 ×

Fot. 4. Charakterystyczny kryształek węglika krzemu obserwowany na powierzchni taśmy krzemowej. SEM. pow. 2500 ×

Fot. 5. Zaburzenie równomiernego kształtu taśmy obserwowane na jej bocznej powierzchni, utworzone w wyniku obecności w taśmie poprzecznej granicy bliźniaczej. SEM, pow. 100 ×

Fot. 6. Mikrorowki powstałe na płaskiej powierzchni taśmy przy dużych szybkościach wzrostu

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Войцех ЯКУБИЦКИ, Ежы КОНЦКИ

ИССЛЕДОВАНИЯ ДЕФЕКТОВ МОНОКРИСТАЛЛИЧЕСКИХ КРЕМНИЕВЫХ ЛЕНТ, ПОЛУЧЕННЫХ МЕТОДОМ EFG

Резюме

В статье приведена характеристика структуры кремниевых лент, получаемых в Польше методом EFG. В полученных кристаллах обнаружено наличие двойниковых границ, двойниковых ламелей, дислокаций, высоко и низкоугольных границ зерен. На образование приведенных дефектов существенное влияние имеет применение графита как материала на матрицы.

ОБЪЯСНЕНИЕ ФИГУРЫ

Фиг. 1. Зачаток процесса кристаллизации кремниевых лент методом EFG
1 — матрица, *2* — капилляр, наполненный жидким кремнием, *3* — пленка жидкого кремния, *4* — кристалл, *5* — зародыш; *a* — наполнение капилляра жидким кремнием, *b* — соприкосновение зародыша с пленкой жидкого кремния, разлитой на поверхности матрицы, *c* — образование сужения (шейки), *d* — расширение кристалла при увеличении скорости вытягивания

ОБЪЯСНЕНИЕ ФОТОГРАФИЙ

Фот. 1. Фрагмент сильно дефермированной структуры кремниевой ленты
1 — скопления дислокации, *2* — двойниковые ламели, *3* — дислокационные воронки, расположенные в линии. Увел. 50 ×

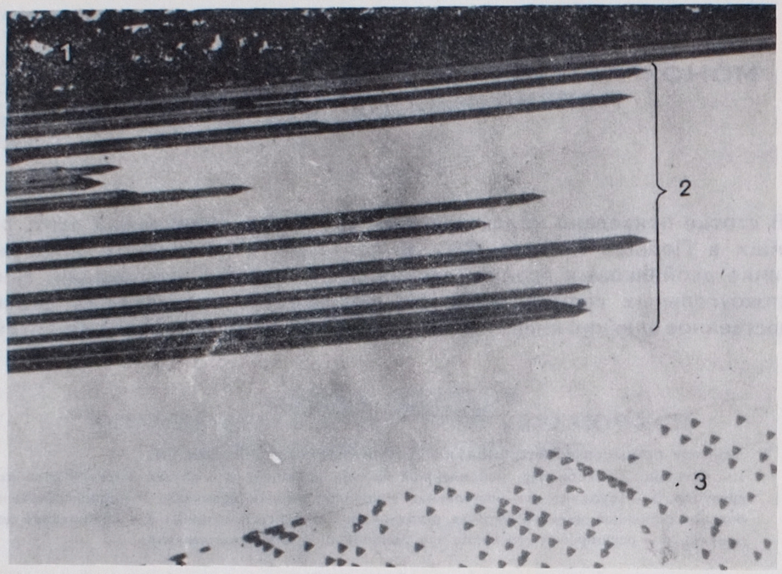
Фот. 2. Ряд параллельных, расположенных вдоль кристалла двойниковых границ, видимых в изломе (с левой стороны) и на поверхности ленты (с правой стороны фотографии). СЭМ. Увел. 100 ×

Фот. 3. Двойникоые ламели и ряд широкоугольных границ зерен, появившихся в результате наличия включений графита в пленке жидкого кремния. СЭМ. Увел. 250 ×

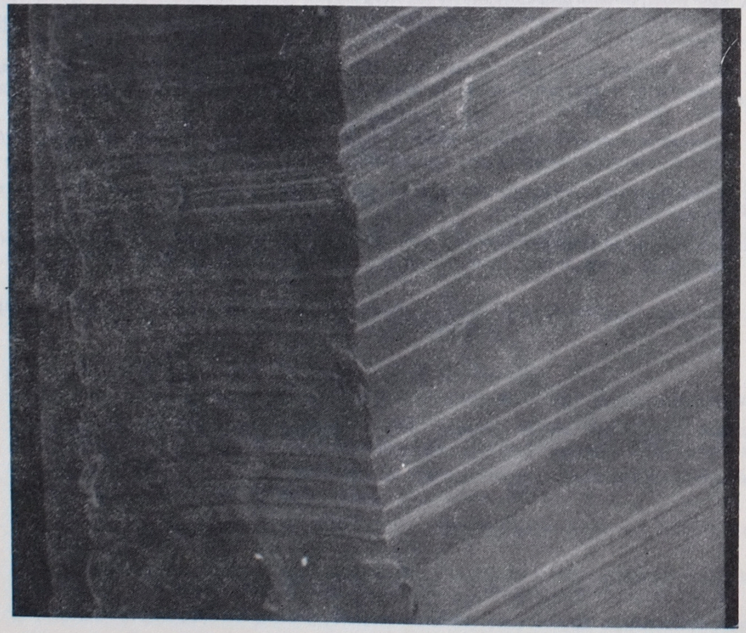
Фот. 4. Характерный кристаллик карбида кремния, наблюдаемый на поверхности кремниевой ленты. СЭМ. Увел. 250 ×

Фот. 5. Нарушение равномерной конфигурации ленты, наблюдаемое на ее боковой поверхности, возникшее в результате присутствия в ленте поперечной двойниковой границы. СЭМ. Ув. 100 ×

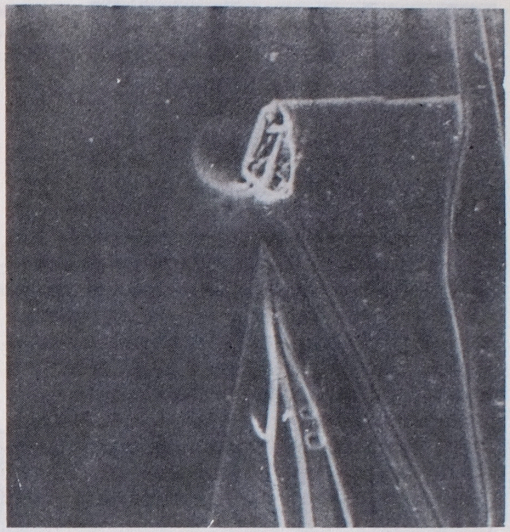
Фот. 6. Микроканавки образовавшиеся на плоской поверхности ленты при больших скоростях роста



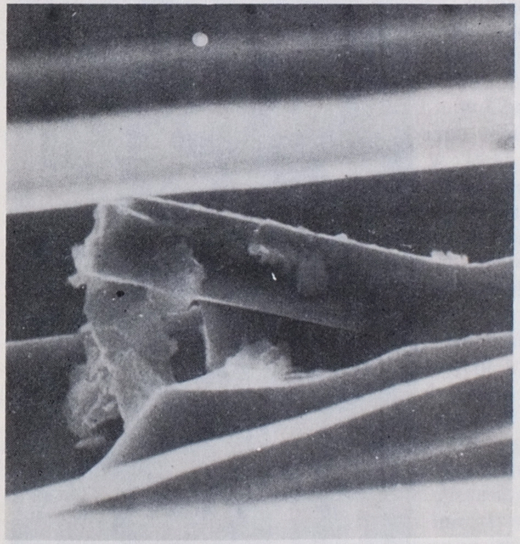
Phot. 1. A fragment of defect structure of the silicon ribbon
1 – dislocation pile-ups, *2* – twin lamellae, *3* – dislocation etch pits arranged in lines. × 50



Phot. 2. A series of parallel twin boundaries running along the crystal, observed in the fracture (left part) and at the ribbon surface (right part). SEM, × 100

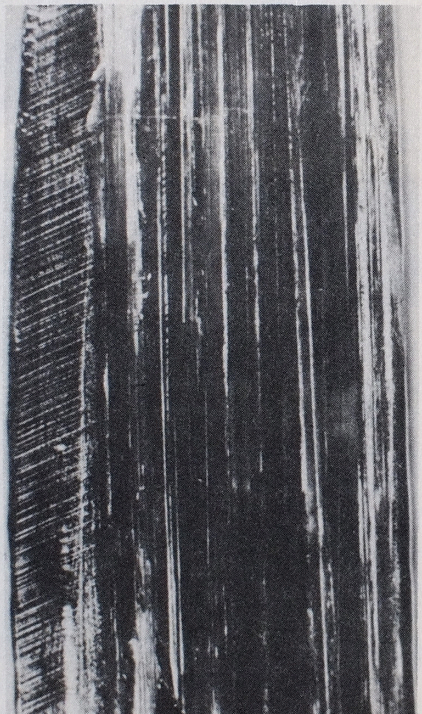


Phot. 3. Twin lamellae and high-angle grain boundaries owing their origin to the presence of graphite inclusion in the liquid silicon layer SEM, × 260



Phot. 4. A characteristic silicon carbide crystal observed at the silicon ribbon surface. SEM, × 2500

Phot. 5. Disturbance of the regular shape of ribbon observed at its lateral surface, due to the presence of a transverse twin boundary in the ribbon. SEM, × 100



Phot. 6. Ridges formed at the flat ribbon surface at high growth rates