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*RESEARCH ARTICLE / ARAŞTIRMA MAKALESI*

# Structural and Nanomechanical Properties of Silicon Single Crystals Grown by the Czochralski Method

# Czochralski Metodu ile Büyütülen Silisyum Tek Kristalinin Yapısal ve Nanomekanik Özellikleri

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## Abstract

The rapid advancements in the fields of artificial intelligence, cloud computing, big data analysis and internet of things have expanded the use of electronic devices and increased the demand for semiconductors. The Czochralski method, the most common and effective production technique for these materials, allows the production of single-crystal forms of elements such as Silicon (Si), Germanium (Ge), and various semiconductor compounds. In this study, the crystal structure, surface morphology and mechanical properties of a Si wafer, prepared by slicing a single crystal Si ingot grown by the Czochralski method, were determined by x-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and nanoindentation methods, respectively. XRD analysis of the silicon wafer confirmed its single-crystal structure, showing a cubic lattice structure and a single peak on the (100) plane, while SEM and AFM analyses determined that the surface is smooth, even, and undamaged. Hardness and elastic modulus values for the Si wafer, calculated from indentation tests using a Berkovich tip under different loads, were determined to be an average of 19 GPa and 255 GPa, respectively. These results hold vital importance for the advancement of semiconductor technologies. The design and production of electronic devices with superior performance and durability can be achieved with a comprehensive understanding of the mechanical properties of the materials.

***Keywords:*** *Silicon single crystal, Czochralski method, Nanoindentation, Hardness*

## Öz

Yapay zeka, bulut bilişim, büyük veri analizi ve nesnelerin interneti alanlarındaki hızlı gelişmeler, elektronik cihazların kullanımını genişletmiş ve yarıiletkenlere olan talebi artırmıştır. Bu malzemelerin üretiminde en yaygın ve etkili yöntem olan Czochralski yöntemi, Silisyum (Si), Germanyum (Ge) gibi elementlerin ve çeşitli yarı iletken bileşiklerin tek kristal formunda üretilmesine olanak sağlar. Bu çalışmada, Czochralski yöntemi ile büyütülen silisyum tek kristal ingottan kesilerek hazırlanan Si plakanın (wafer) kristal yapısı, yüzey morfolojisi ve mekanik özellikleri sırasıyla x-ışınları kırınımı (XRD), taramalı elektron ve atomik kuvvet mikroskobu (SEM ve AFM) ve nanoindentasyon yöntemi ile tespit edilmiştir. Silisyum plakanın XRD analizi, kübik kafes yapısını ve (100) düzleminde tek bir pik göstererek tek kristal yapısını doğrularken, SEM ve AFM analizleriyle, yüzeyin düzgün, pürüzsüz ve hasarsız olduğu belirlenmiştir. Farklı yüklerde Berkovich tip uç kullanılarak yapılan indentasyon testleri sonucunda Si plakaya ait sertlik ve elastisite modülü değerleri ortalama 19 GPa ve 255 GPa olarak hesaplanmıştır. Bu sonuçlar, yarıiletken teknolojilerin ilerlemesi için hayati öneme sahiptir. Üstün performans ve dayanıklılığa sahip elektronik cihazların tasarımı ve üretimi, malzemelerin mekanik özelliklerinin kapsamlı bir şekilde anlaşılmasıyla gerçekleştirilebilir.

***Anahtar Kelimeler:*** *Silisyum tek kristal, Czochralski yöntemi, Nanoindentasyon, Sertlik*

## 1. Introduction

Single crystal silicon is the most commonly used semiconductor material as a substrate in microelectronics and optoelectronic applications. The growth technology of single crystal silicon has made rapid progress in recent years. The process of crystal growth is essentially an interdisciplinary field involving metallurgy and materials engineering, mechanical engineering, chemical engineering, physics, and so on [1]. The requirement for bigger wafer diameters and the desire to increase the mass quality of crystals are the driving forces behind the development of silicon crystal growth technology. [2]. Single crystal materials exhibit superior properties compared to polycrystalline or amorphous equivalents. There are generally two main groups in the methods of growing single crystals, which are growth from solution and growth from melt. The methods used in growth from melt are also known as the Czochralski, Bridgman-Stockbarger, and Verneuil methods, named after their inventors [3,4]. Jan Czochralski invented the Czochralski method of single crystal formation in 1917 [5]. Despite being a rapid growth technique, Czochralski is frequently employed in optical applications for semiconductors and oxide/fluoride materials. This method

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allows for the production of excellent and homogeneous crystals. The Czochralski crystal growth technique is a melt growth technique that involves the solidification of a liquid phase [6]. Since the melting point of silicon is 1412°C, the furnace is heated above 1500°C. A diminutive seed crystal, possessing the requisite crystallographic orientation, is submerged into the liquefied silicon. Subsequently, it is gradually retracted by the mechanism designed for crystal extraction. In the pursuit of fabricating a monocrystalline ingot, the preservation of homogeneity is paramount. This is accomplished by concurrently rotating and extracting the seed crystal. In contrast, the furnace is subjected to a rotation counter to the direction of the crystal puller. As the molten silicon adheres to the seed crystal and is retracted, it commences solidification, mirroring the orientation of the seed crystal. As a result, a monocrystalline ingot is successfully procured. In the event that a doped crystal is required, dopant material is infused into the molten silicon, thereby enabling its integration into the burgeoning crystal lattice. The withdrawal rate, as well as process controls such as the rotation speed of the crystal puller, are crucial for obtaining high-quality single crystals. Si-based MEMS technologies commonly utilize Si wafers oriented in the [100] direction. In other words, the surface of the Si wafer is the (100) crystallographic plane. Less frequently, wafers oriented in the [111] or [110] directions are used [7].

The progression of Microelectromechanical Systems (MEMS) technology has necessitated the appraisal of the mechanical attributes of semiconductor Si plates and their associated thin films. These components are integral to the structural integrity of the devices, thereby ensuring their reliability. Over the years, a multitude of testing methodologies have been devised to scrutinize the mechanical properties of these materials, which can be broadly categorized into direct and indirect techniques. Direct methodologies encompass a spectrum of tests, including tensile, bending, and compression tests. These techniques offer a straightforward approach to deciphering the stress-strain relationships inherent in Si plates, bearing a resemblance to traditional testing methodologies employed for bulk materials. However, the implementation of such tests on Si plates is fraught with challenges due to their inherent brittleness and extreme sensitivity to the minutest of defects. Additional complexities associated with this approach include the fabrication of test-suitable plates and the difficulties encountered in their gripping, manipulation, and alignment. To circumvent these challenges, indirect methodologies, such as nanoindentation testing, have been developed. This technique provides a reliable avenue for assessing the mechanical properties of surface layers of bulk materials, inclusive of the thin films that are deposited on Si plates. It offers consistent measurements of parameters such as hardness, elastic modulus, and fracture toughness. A significant advantage of this methodology is its simplicity, obviating the need for intricate sample preparation [8].

Indentation is a non-destructive testing method used to determine mechanical properties. A rigid and non-deformable penetrating tip (indenter) is used to apply a mechanical load (P, load) to the surface of the material to be tested. This loading results in a permanent indentation mark on the material. In nanoindentation technique, it is possible to determine the mechanical properties of thin films and small-scale materials such as hardness and elastic modulus by creating smaller indentation depths with smaller loads. A loading-unloading curve, which represents the characteristic behavior of the material depending on the applied load (P) and the indentation depth (h), is created, and the mechanical properties are calculated based on this curve. In the domain of material science, the advent of the nanoindentation technique can be traced back to the mid-1970s. Nevertheless, it was the pioneering research conducted by Oliver and Pharr, employing a Berkovich-type indenter, that ignited an unprecedented wave of interest in probing the hardness and elastic modulus of materials at a minuscule scale. This technique of mechanical testing has demonstrated its efficacy in deciphering the complex mechanical behavior of a diverse spectrum of materials, encompassing ceramics, composites, alloys, coated surfaces, and thin films [9-11]. It is imperative to underscore that the mechanical attributes of the silicon substrate not only govern the mechanical performance of the device, but also significantly impact its electrical and optical characteristics [12]. In this study, the mechanical properties such as hardness and elastic modulus of a single crystal silicon wafer produced by the Czochralski method were determined using a nanoindentation device at different loads.

## 2. Materials and Methods

The undoped single crystal Si ingot used for nanomechanical studies was grown at the PVA Tepla Czochralski laboratory-scale single crystal ingot growth machine located at Dokuz Eylül University, Center for Electronic Materials Production and Application (EMUM) (Figure 1). The materials and specifications required for the preparation of Si single crystal plates are given in Table 1.

The schematic diagram illustrating the growth of a single crystal silicon ingot is shown in Figure 2. The process consists of loading polycrystalline silicon, melting, shoulder, neck, body, and cone formation stages. After loading the polycrystalline silicon into the quartz crucible, the melting process was conducted at a temperature of 1560 °C. Once the molten silicon reached a homogeneous structure, a [100]-oriented single crystal seed silicon was immersed into the molten silicon pool at the solid-liquid phase equilibrium temperature of 1427 °C, and the formation of neck and shoulder was observed in the crystallization process. Upon reaching the desired diameter for shoulder formation, the pulling and rotation speeds were adjusted to proceed to the body formation stage. The ingot production was completed by varying the parameters of temperature, rotation, and pulling speeds. The entire process took approximately 18 hours, resulting in the production of an undoped single crystal Si ingot with dimensions of 300 mm in length and 110 mm in width [13].

**Table 1**. Materials and properties for the manufacture of single-crystal silicon wafers

| Aim | Materials | Properties |
|---|---|---|
| Czochralski process (Ingot production) | Polycrystalline silicon (Si) | Pure silicon (99.9999%), loaded 5 kg. |
| | Crucible | Polished Quartz ($SiO_2$) crucible |
| | Argon gas | 99.999% purity, 50 L, 3 tubes were used. |
| Wafer preparation (ingot slicing, lapping, polishing and cutting) | Colloidal alumina | 9 µm $Al_2O_3$ + deionized water (1/10), cast plate surface [Lapping] |
| | Colloidal cerium oxide | 3 µm $Ce_2O_3$ + deionized water (1/10), cast plate surface [Lapping] |
| | Colloidal nano silica | Nano $SiO_2$ (40 nm) + deionized water + $H_2O_2$ on pad surface [Polishing] |

**Figure 1.** PVA Tepla Czochralski laboratory scale single crystal ingot growth device [13].

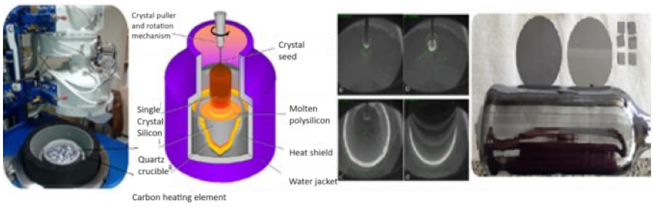


**Figure 2.** Schematic diagram of the Czochralski crystal growth process [13].

The single crystal Si ingot obtained after the Czochralski process underwent slicing, lapping, polishing, cutting, and cleaning processes using the materials listed in Table 1. The ingot slicing process was performed using a precision slicing machine (STX 1202) with the assistance of a diamond particle-coated wire. Lapping and polishing procedures were conducted on a Logitech machine, where the Si wafer was placed on a casting substrate to achieve desired smooth and flat surfaces. In these processes, $Al_2O_3$ and $CeO_2$ powders, as well as $SiO_2$ suspension, were utilized [13]. The polished Si wafers were subsequently cut into 20mm x 20mm squares, as shown in Figure 2. Following each stage, the samples were cleaned in acidic and alkaline baths, rinsed, and dried. The obtained square cross-section Si samples were subjected to various structural and mechanical tests.

The Thermo-Scientific ARL X'TRA model X-ray diffraction (XRD) instrument was used to determine whether the samples were single crystals after magnification and to explore their phase structure. The analysis was conducted using monochromatic Cu-Kα X-ray radiation (λ=1.54055 Å) at voltage of 45 kV and current of 44 mA, with a scanning rate of 2 °/min and angles ranging from 2θ=10-75°. The surface morphology of the samples was examined using a COXEM EM-30 scanning electron microscope (SEM) and a Nanosurf easyScan 2 atomic force microscope (AFM).

The IBIS nanoindentation device was used to determine the hardness and elastic modulus of the silicon substrate. Prior to testing, calibration tests were performed on a fused silica reference sample. Nanoindentation tests were conducted on the substrate surface at ten different loads (30-300 mN), and loading-unloading curves were extracted from the results to calculate the values of hardness and elastic modulus.

## 3. Result and Discussion

### 3.1. Crystalline Structure and Phase analysis

The XRD pattern of the sliced plate from a single crystal Si ingot produced by the Czochralski method is shown in Figure 3. Crystal orientation is examined in XRD analysis to determine if a material is a single crystal. Polycrystalline silicon with a cubic lattice structure (JCPDS 27-1402) contains crystals on different planes [14] However, the single crystal silicon plate produced by the Czochralski process exhibited a single peak at 69.46° on the (100) plane. This indicates that all planes of the produced ingot are oriented in a single direction, confirming it is a single crystal. As can be seen from the figure, no other peaks were observed. This is supported by the literature [15-18].

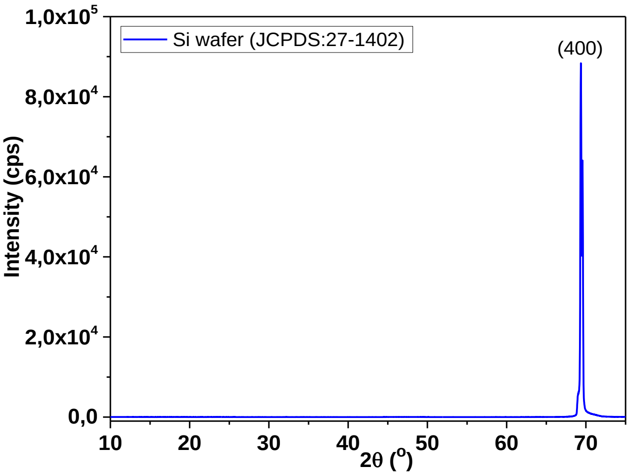


**Figure 3.** XRD pattern drawing and phase analysis of a single crystal Si wafer.

### 3.2. Surface Morphology

Surface roughness, morphology, and topography are important factors for Si substrates and thin films. In principle, these factors strongly influence the surface coating quality. In this regard, SEM (surface morphology and topography) and AFM (surface morphology and roughness) images of Si plates are discussed in Figure 4. Figure 4a shows a secondary electron image of the Si plate taken at a magnification of 1000X under a 20 kV accelerating voltage after the polishing process. Upon examining the morphology, it can be observed that the surface is smooth, polished, and free of any scratches or cracks. Figure 4b presents two- and three-dimensional 20 µm x 20 µm AFM micrographs of the surface. The study conducted for surface roughness and morphology determined linear and areal roughness values of 6 nm and 3.4 nm, respectively. The obtained values indicate that the surface is prepared in an extremely smooth and polished manner. Similar surface images and roughness values have also been reported in the literature [19-20].

### 3.3. Mechanical Properties

The indentation method is a characterization technique in which a rigid, sharp indenter typically made of a mechanically known, extremely hard material like diamond penetrates a homogeneous solid material at a depth of h from the surface under an applied indentation load P. During a loading-unloading cycle, the values of P-h are continuously recorded in a computer environment to characterize the process.

In this study, loading-unloading curves for different loads applied to the wafer are presented in Figure 5a. It has been observed that the indentation depth increases with increasing load (Figure 5b). At the lowest load of 30 mN, this value was measured as 0.302 µm ± 0.013, while at the highest load of 300 mN, it was measured as 1.050 µm ± 0.003. Nanoindentation tests revealed an intriguing observation in the form of a "pop-out" phenomenon that appeared during the unloading phase, indicating the occurrence of inelastic deformation. This behavior can be attributed, as suggested by Vodenitcharova and Zhang's theory, to a sudden volumetric increase resulting from a phase transformation within the material [8].

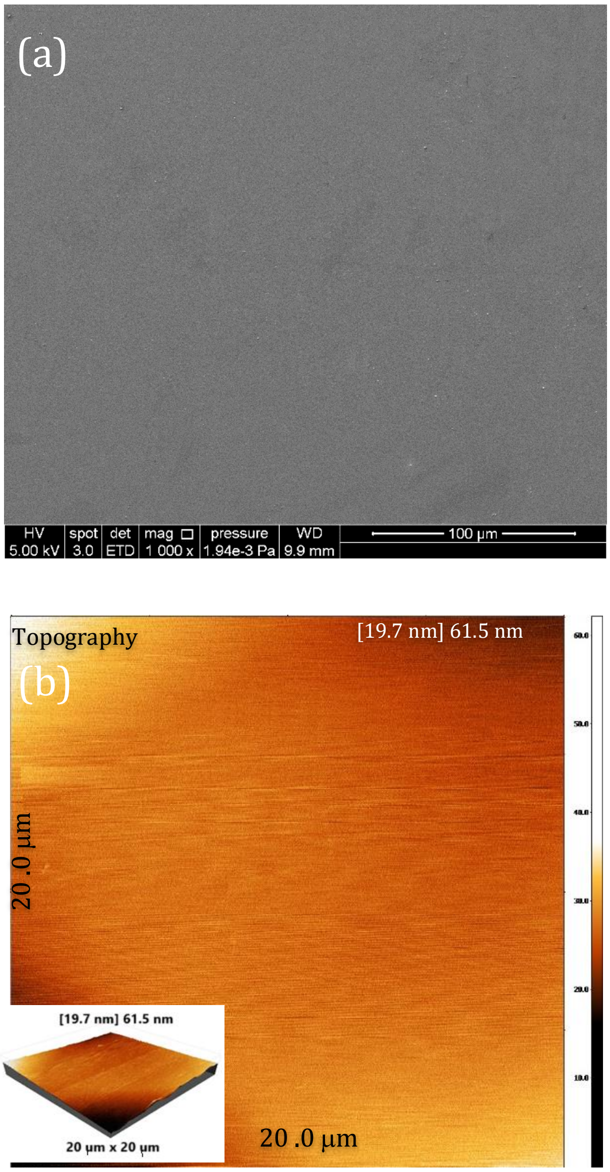
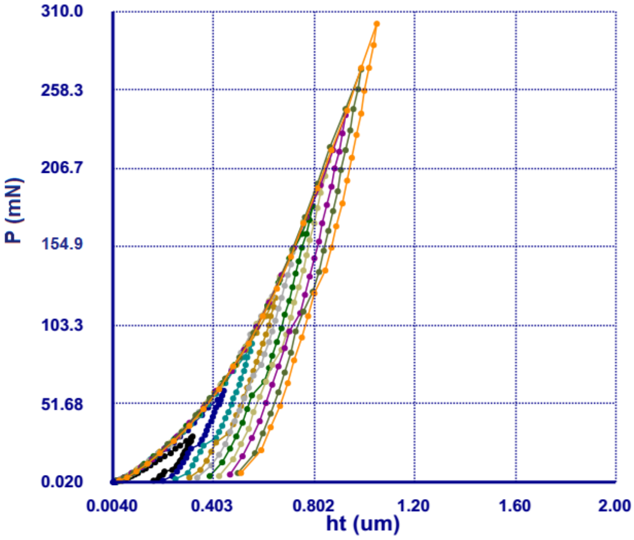


**Figure 4.** Micrographs of a single crystal Si wafer SEM (a) and AFM (b).

The hardness values of the Si plate at different loads obtained from the nanoindentation test are shown in Figure 6. In the measurements conducted, the average highest hardness value at three different loads was determined as 21.8 ± 1.35, while the lowest hardness value was calculated as 18.90 ± 0.24. Based on the result obtained from the graph, we can say that the hardness value of the Si plate is ~19 GPa. It is expected that the hardness result will be higher at lower loads. Given that the Berkovich diamond indenter's practical tip has a finite sharp point radius, the elastic modulus and hardness rise with contact depth at lesser depths. For bulk Si wafers, indentation depth values of 100 nm and more are typically considered to be accurate, especially in light of the potential for the surface to be oxidized [21]. However, the range where the hardness values begin to stabilize provides us with the true result.



| P (mN) | ht (µm)$_{mean}$ |
|---|---|
| 30 | 0,302±0,013 |
| 60 | 0,437±0,004 |
| 90 | 0,551±0,005 |
| 120 | 0,644±0,005 |
| 150 | 0,719±0,004 |
| 180 | 0,795±0,003 |
| 210 | 0,860±0,002 |
| 240 | 0,926±0,003 |
| 270 | 0,982±0,008 |
| 300 | 1,050±0,003 |

**Figure 5.** Loading-unloading curve (a) and Loading-mean penetration values (b) of the silicon wafer.

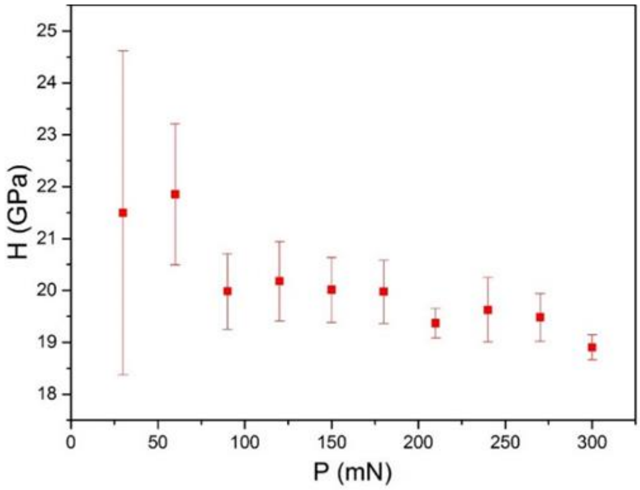


**Figure 6.** Hardness values of silicon wafer at different loads.

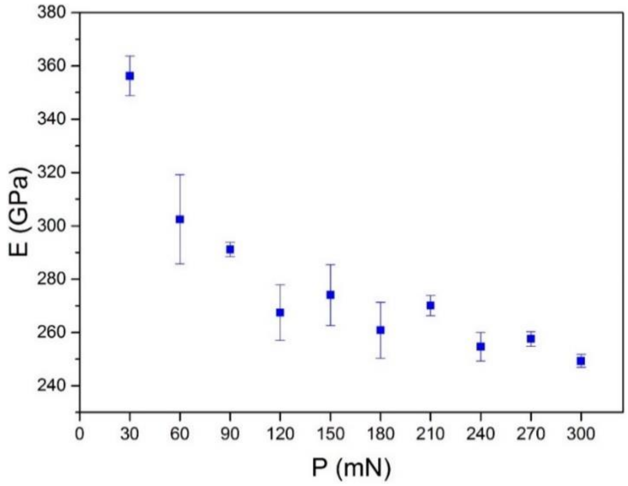


**Figure 7.** Elastic modulus values of silicon plate at different loads.

The results of the nanoindentation test conducted on Si plates at different loads are presented in Figure 7. According to the results, the average highest elastic modulus is calculated as 356 ± 7.4 GPa, while the lowest elastic modulus value is measured as 249 ± 2.3 GPa. The elastic modulus value for the Si plate can be read from the graph to be ~255 GPa.

## 4. Conclusion

This study examined the mechanical properties of plates obtained from single crystal silicon ingots produced by the Czochralski method. These plates are the preferred circuit elements for integrated circuit manufacturing and photovoltaic solar cell production in semiconductor technology. Analyzes conducted using SEM and AFM devices to evaluate the surface quality of the plates have determined that the surface morphology is smooth and uniform. Since surface roughness and morphology are critical factors for surface coatings, these findings indicate a successful surface treatment process. The hardness and elastic modulus of the plates were measured using the nanoindentation technique. This procedure was conducted at 10 different loads ranging from 30 mN to 300 mN. As the load increased, an initial decrease in hardness and elastic modulus values was observed, but the rate of change subsequently decreased. According to the obtained results, the hardness value of the silicon plates was approximately 19 GPa, and the elastic modulus was calculated to be approximately 255 GPa. These findings demonstrate the suitability of such silicon plates for semiconductor and photovoltaic applications. In conclusion, significant findings have been discovered that contribute to the design and production of electronic devices with improved performance and durability, advancing semiconductor technologies.

## Ethics committee approval and conflict of interest statement

This article does not require ethics committee approval. This article has no conflicts of interest with any individual or institution.

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## Author Contribution Statement

All authors contributed equally to the writing, conceptualization, literature review, data collection, validation and critical review of this manuscript.

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